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RECOMMENDED METHODS OF REDUCTION, NEUTRALIZATION, RECOVERY, OR DISPOSAL OF HAZARDOUS WASTE

VOLUME XIII. INDUSTRIAL AND MUNICIPAL DISPOSAL CANDIDATE WASTE STREAM CONSTITUENT PROFILE REPORTS. INORGANIC COMPOUNDS (CONTINUED)

TRW Systems Group

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This volume contains summary information and evaluation of waste management methods in the form of Profile Reports for inorganic compounds. These Profile Reports were prepared for either a particular hazardous waste stream constituent or a group of related constituents. Each Profile Report contains a discussion of the general characteristics of the waste stream constituents, their toxicology and other associated hazards, the definition of adequate management for the waste material, an evaluation of the current waste management practices with regard to their adequacy, and recommendation as to the most appropriate processing methods available and whether the waste material should be considered as a candidate for National Disposal, Industrial Disposal, or Municipal Disposal.

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Industrial Disposal Candidate
Municipal Disposal Candidate
Domestic Bauxite Mud
Trivalent Chromium Salts
Copper, Lead, and Zinc Mill Tailings
Acids
Lead Compounds
Manganese Compounds
Nickel Compounds
Halogenated Phosphorous Compounds
Sodium Compounds
Zinc Compounds
Selenium
Strontium
Thallium
Thallium Sulfate
Potassium Compounds
Taconite Tailings

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Under Section 212 of Public Law 91-512, the Resource Recovery Act of 1970, the U.S. Environmental Protection Agency is charged with preparing a comprehensive report and plan for the creation of a system of National Disposal Sites for the storage and disposal of hazardous wastes. The overall program is being directed jointly by the Solid and Hazardous Waste Research Laboratory, Office of Research and Development, National Environmental Research Center, Cincinnati, and the Office of Solid Waste Management Programs, Office of Hazardous Materials Control. Section 212 mandates, in part, that recommended methods of reduction, neutralization, recovery, or disposal of the materials be determined. This determination effort has been completed and prepared into this 16-volume study. The 16 volumes consist of profile reports summarizing the definition of adequate waste management and evaluation of waste management practices for over 500 hazardous materials. In addition to summarizing the definition and evaluation efforts, these reports also serve to designate a material as a candidate for a National Disposal Site, if the material meets criteria based on quantity, degree of hazard, and difficulty of disposal. Those materials which are hazardous but not designated as candidates for National Disposal Sites, are then designated as candidates for the industrial or municipal disposal sites.

A. W. Breidenbach, Ph.D., Director
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PROFILE REPORT

Domestic Bauxite Mud (282) and Foreign Bauxite Mud (283)

1. GENERAL

Bauxite is a heterogeneous material composed principally of the aluminum oxide minerals, gibbsite [$Al\ (OH)_3$], a trihydrate [$Al_2O_3 \cdot 3H_2O$], and the monohydrates, backmite [$AlO(OH)$], and diaspore [$HAlO_2$]. Major impurities in the bauxite ores are iron oxides, aluminum silicates, and titanium oxides.[1975,2492]

Bauxite is normally refined by the Bayer process. This process involves leaching the bauxite with caustic at elevated temperatures and pressures, followed by the separation of the resulting sodium aluminate solution and the selective precipitation of alumina [$Al_2O_3 \cdot 3H_2O$].

The residue, or tailings from this process is commonly called "red mud." In the case of some ores, the tailings, "red mud", are further treated to extract the aluminum silicates and the residuals from this process are known as "brown mud."

The alumina is further treated by electrolysis in a molten bath of cryolite [$3NaF \cdot AlF_3$] to produce primary aluminum.

The primary bauxite ores of concern are Jamaican, Surinam and Arkansas. "Jamaican ore is a mixture of both trihydrate and monohydrate materials, and this type contains about 50% Al_2O_3, 1 to 2 percent silica, and 20 to 30 percent ion oxide. The Surinam type is mainly the trihydrate gibbsite usually containing 50 percent or more Al_2O_3, 2 to 15 percent silica, and 5 to 15 percent iron oxide."[1975] The Arkansas ores are lower in iron oxides and higher in aluminum silicates since they were formed from the weathering of nepheline syenite.

The concentrate from the processing of the ores is in all cases alumina for further processing to primary aluminum.

Tailings from the process have chemical compositions as delineated below:[0146]

Bauxite Source	Residue Type	Composition-Percent					
		Al_2O_3	Fe_{2-4}	TiO_2	SiO_2	Na_2O	CaO
Jamaica	Red Mud	20	47	6	--	4	5
Surinam	Red Mud	20	25	10	--	10	6
Arkansas	Brown Mud	9	8	3+	17	5	40

These tailings are all quite fine, indeed one Jamaican red mud sample had an average grain size between 0.5 and 2.0 microns with some agglomerated particles to 10 microns. The Jamaican tailings are normally flocculated by the addition of starch and dewatered by settling in thickeners, even so the final residue has a solids content of only 20 percent. The other tailings, though filterable, are also quite fine.

The major areas of production of alumina plant wastes are the lower Mississippi River, on the gulf coast, and in Arkansas. Some 7 million tons of tailings are generated annually in these areas.

2. TOXICOLOGY

Bauxite tailings constitute a negligible toxicological hazard.

3. OTHER HAZARDS

Although not presenting a toxicological problem, bauxite tailings constitute an environmental problem on the basis of two major elements: (1) the sheer volume of the refuse materials; (2) the dust problems encountered because of the fineness of the tailings when they are finally dewatered.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Bauxite tailings are presently disposed of by collection in tailings ponds (see Profile Report on Copper, Lead and Zinc tailings) or by direct discharge into the Mississippi River.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Of the two disposal methods described in Section 4 of this report, only that of ponding is judged to be an acceptable method. The discharge to tailings into large potable water sources has not been proven an acceptable method of disposal and should be curtailed until the environmental effects of this practice are determined.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Because of the negligible toxicological effect, bauxite tailings are not considered candidates for National Disposal Sites.

The United States Bureau of Mines[0146] has done considerable work in extracting mineral values from the "red mud" residues. However, the major volume of material will remain to constitute an environmental hazard. In addition to the recommendations for research and development to alleviate the environmental effects contained in the Profile Report on Copper (275), Lead and Zinc (276), the development of more effective flocculants would be most useful in providing a viable alternative to dumping tailings into the Mississippi River.

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PROFILE REPORT

Chlorates with Red Phosphorus (516)

1. GENERAL

Potassium chlorate is a very powerful oxidizing agent which in admixture with combustible materials forms a number of powerful explosives. Red phosphorus, a reducing material, is used in some of these explosive compositions. Mixtures used in toy pistol caps and toy torpedoes contain both potassium chlorate and red phosphorus. Two examples of these mixtures are as follows: (1) 67 parts potassium chlorate, 27 parts red phosphorus, 3 parts sulfur, and 3 parts calcium carbonate bound with an unspecified amount of "gum water", and (2) 61 parts potassium chlorate, 4 parts red phosphorus, 21 parts black antimony sulfide, 2 parts calcium carbonate, and 12 parts animal glue.[2169]

The physical/chemical properties for potassium chlorate and red phosphorus are summarized on the attached worksheets.

2 TOXICOLOGY

Potassium chlorate, like sodium chlorate (see Profile Report on Sodium Chlorate [385]) is not highly toxic, but ingestion or excessive inhalation of dust should be avoided. Prolonged exposure to chlorate dust may cause skin irritation to the mucous membrane of the eyes, nose and throat.[2123] Red phosphorus is considered relatively non-poisonous and is much less reactive than white phosphorus. The other components of these mixtures are generally considered non-poisonous.

3. OTHER HAZARDS

Potassium chlorate and red phosphorus mixtures, when confined, are sensitive to electrical discharge, heat, friction, and impact. They undergo detonation when subjected to a very mild electrical, mechanical or thermal shock from a spark, flame or percussion. These mixtures cannot be stored under water prior to use because potassium chlorate is soluble and will be extracted from the mixture.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Relatively small quantities of cap and torpedo mixtures are manufactured. They are not shipped prior to formulation into the end products. The sensitivity of these mixtures requires that excess and scrap material from fireworks charging operations be stored under water until destroyed by burning. Caps are described as "toy caps" and are shipped according to Department of Transportation (DOT) regulations for Explosives, Class C,[2170] if the individual caps each contain less than 0.25 grains of the explosive mixture. "Torpedoes, cap" are commonly packed in sawdust in pasteboard cartons and are described as special fireworks. They are shipped as Explosives, Class B[2382] if they contain less than 1/2 grain of $KClO_3$ - P mixture, or less than 4 grains of $KClO_3$, Sb_2S_3 and P mixture.

The safe disposal of potassium chlorate-phosphorus mixtures is defined in terms of the recommended provisional limits in the atmosphere and in water and soil environments. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Phosphorus, red	0.001 mg/M^3*	0.01 TLV*
Contaminant in Water and Soil	**Provisional Limit**	**Basis for Recommendation**
Phosphorus, red	0.005 mg/l*	Stokinger & Woodward Method

*Estimated from data for white phosphorus

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Detonator Destruction Furnace

The approved method referenced in the Ordnance Safety Manual for the destruction of detonators and primers may be used for torpedoes containing chlorate-phosphorus mixtures. In this method the components are fed to the combustion chamber of a specially designed detonator destruction furnace by means of a channel chute and a special conveying device.[2170] Scrubbers are employed to remove toxic fumes and dusts such as NO_x, P_4O_{10}, HCl, SO_2, and metal oxides.

Option No. 2 - Burning Pit Detonation

Torpedoes and caps in large quantities are detonated by burning in pits by applying heat from a fire. The devices are placed on top of a flammable substance such as straw and the flammable substance is ignited by means of a squib. Other explosives must be kept behind a barricade with overhead protection during destruction operations and located at a distance that assures safety. Personnel should be similarly shielded.[1147,2170] This destruction process is not satisfactory because individual components may not detonate and will constitute a personnel hazard during clean-up and because NO_x, metal oxides, P_4O_{10}, SO_2 and hydrogen chloride will be liberated during the destruction process on an uncontrolled basis.

Option No. 3 - Controlled Incineration (Municipal and Plant Incinerators)

Potassium chlorate mixtures, toy torpedoes and toy caps which have been properly marked to permit due precautions in handling can be destroyed safely by burning in municipal or plant incinerator systems equipped with scrubbing and mist removal systems. The incinerators should be fed by automatic conveyor devices, and the scrubber effluent should be neutralized and processed in a standard secondary treatment sewage system before discharge. This technique is recommended for disposal of the mixtures and devices.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Plants manufacturing torpedoes and caps which contain potassium chlorate and red phosphorus mixtures have facilities for the disposal of such mixtures. Devices which are not processed for disposal at such manufacturing facilities are not candidates for National Disposal Sites. The process to be employed for disposal should be Option No. 3, as recommended in Section 5. Surplus, scrap or obsolete materials should be handled by experienced plant personnel or other qualified ordnance demolition personnel.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Phosphorus, red (516)

IUC Name

Common Names

Structural Formula

P_4

Molecular Wt. 124.08 (1)   Melting Pt.   Boiling Pt.

Density (Condensed) 2.34 g/cc @ 20 C (1)   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point   Autoignition Temp. 260 C

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility (1)

Cold Water Insoluble   Hot Water Insoluble   Ethanol Insoluble

Others: Insoluble all solvents

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification flammable solid (1)   Coast Guard Classification inflammable solid yellow label

Comments

References (1) 1416

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Potassium Chlorate (516)

IUC Name Potassium Chlorate

Common Names

Structural Formula

$KClO_3$

Molecular Wt. 122.55 (1)

Melting Pt. 368 C (1)

Boiling Pt. decomposes (1) 400 C

Density (Condensed) 2.337 g/cc @ 20 C (1)

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@

@

@

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility (1)

Cold Water Soluble

Hot Water Soluble

Ethanol Slightly soluble

Others:

Acid, Base Properties

Highly Reactive with reducing substances (1)

Compatible with

Shipped in drums (1)

ICC Classification oxidizing material (1)

Coast Guard Classification oxidizing material (1)

Comments

References (1) 1416

PROFILE REPORTS ON
THE TRIVALENT CHROMIUM SALTS

Chromic Fluoride (485), Chromic Sulfate (486), Chromium Cyanide (487)

1. GENERAL

The salts of trivalent chromium, Cr III, are moderately poisonous materials. Of the three compounds in this Profile Report, only two have any commercial significance. They are chromic fluoride, CrF_3, and chromic sulfate, $Cr_2(SO_4)_3$. Chromium cyanide is not believed to exist at all; a fact to be detailed later. Chromic fluoride was found to have some uses in the textile industry as part of the dyeing operation. Chromic sulfate is extensively used in the leather tanning and finishing industry in a modified, basic form.

Chromic Sulfate

Normal chromic sulfate, $Cr_2(SO_4)_3$ is of no commercial importance, but the so-called basic chromic sulfates are produced in large amounts for use in the leather tanning industry, and are incorporated in various proprietary chrome tan mixtures. These basic chromic sulfate tanning solutions can either be made commercially and supplied to the tanning industry or be prepared directly in the tanning vats. The normal preparation process is the reduction of a sodium dichromate solution with either an organic material (Equation No. 1) or sulfur dioxide (Equation No. 2).[2055] The organic reduction using crude molasses, corn sugar, and sometimes even sawdust is the older and more widely used method. Sulfur dioxide, when used, plays the dual role of reducing agent and, upon oxidation, of furnishing the required sulfate. If sugar is used, sulfuric acid must be added.

$$8Na_2Cr_2O_7 + 24H_2SO_4 + C_{12}H_{22}O_{11} \rightarrow 16Cr(OH)SO_4 + 8Na_2SO_4 + 27H_2O + 12CO_2 \quad (1)$$

$$Na_2Cr_2O_7 + 3SO_2 + H_2O \rightarrow 2Cr(OH)SO_4 + Na_2SO_4 \quad (2)$$

The actual composition of the product is much more complicated than that indicated by the formulas shown. The chromic sulfate produced by these reactions is described as one-third basic since, stoichiometrically, only two-thirds as much sulfate is combined with the chromium as in the normal sulfate. A whole range of basicities is available to the tanning industry for different types of tanning. The production of basic chromic sulfate is performed on a batch basis, and if prepared at the tannery, the hides are added to the same vat in which the reduction took place. No purification of the commercial product is performed before it is spray dried and packed. It is believed that the manufacture of basic chrome sulfate results in no significant amounts of contaminated waste solids or liquids.

The actual chrome tanning of the hides however does create very large amounts of chromic sulfate wastes in aqueous solution resulting from the tanning and subsequent washing of the hides. Hide tanning, by definition, essentially consists of removing organic matter from the hides,thus preserving them. This organic matter, if allowed to build up in the chrome tanning solutions would interfere with the tanning process. Therefore the solutions are normally dumped after being used once or possibly twice. There are incomplete details on some tanneries that are renewing their chrome tanning solutions with more concentrated chromic sulfate rather than dumping the spent tanning solutions. They claim that some chromium tanning solutions are being reused as many as 15 times without detrimental effects. This situation is currently the exception and not the rule.[0087]

An additional, proposed chrome sulfate conservation technique is to precipitate chromium hydroxide from the chrome tanning solutions, filter it,and then redissolve it with sulfuric acid. This technique can remove some of the organic water and allow reuse but most tanners consider the process to be economically impractical and the greater proportion of the tanneries are only using their tanning solutions once.

Very little waste stream segregation is performed in the tanning industry and the 2 to 12 ppm trivalent chrome concentration in the diverse mixture of brines, fat, acids, and large amounts of rinse water constitute a fairly typical waste stream. The majority of tanneries are located in or near large metropolitan areas to permit the utilization of municipal or joint water treatment facilities.[0087] The cities are always the meat packing centers, i.e., Chicago, Milwaukee, or Los Angeles. It is estimated that 80 percent of the tanning wastes are being discharged to sewers for treatment by municipal waste water treatment plants. The remaining 20 percent are being treated in onsite plants for solids and BOD reduction before discharge to sewers or waterways. The quantity of trivalent chromium in inadequately treated tannery effluents discharged to open waterways, if any, was not determined because of the obvious difficulties in obtaining such sensitive information, but it is expected that future tightening of discharge limits will result in no discharge from tanneries into open waterways.

Chromic Fluoride

Chromic fluoride is used in the textile industry as a dyeing aid and mordant. Other trivalent chrome compounds can be used in its place. The constantly changing processes in the textile industry as well as the free substitution of different chemicals for process applications makes it difficult to determine exactly how much chromic fluoride is being used, but it is believed that its consumption is very small.[2053,2054,2055]

The completely anhydrous chromic fluoride is insoluble and is not used in the textile trade. Two hydrated compounds are commercially available. They are $CrF_3 \cdot 4H_2O$ and the more soluble $CrF_3 \cdot 9H_2O$. These compounds and their basic, complex compounds are used as mordants for wool, in aftertreating oxidation sensitive direct cotton dyes, and with special mordant acid dyes in the printing of worsted woolen. It has also been stated that chromic fluoride imparts some moth-proofing qualities.[2055]

When used, chromic fluoride is contained in vats and is exhaustively deposited on the textile that is either dipped or run through continuously. A significant portion of solution is lost by transfer to subsequent rinsing and post treatment tanks.

The chrome wastes from textile mills are characteristically mixtures of the effluents from many different processes and contain 1 to 100 ppm trivalent chromium. Most of the Southern mills have some sort of on-site water treatment facilities whereby chromium and other heavy metal wastes are removed by precipitation through pH adjustment techniques. An official of the American Association of Textile Chemists and Colorists indicated that virtually all of the Southern mills have responded to the needs for some water treatment. They either operate their own on-site water treatment facilities or are cooperating with a neighboring city for joint municipal treatment. The Northern textile mills, benefiting from the greater availability of water, are characterized as normally sewering their trivalent chromium wastes and diluting it as required for municipal treatment.[1480]

Chromium Cyanide

No references to chromium cyanide could be found in the literature except for a brief discussion of chrome cyanide compoundy by Udy.[2055] Chromous cyanide and chromic cyanide are products of reactions under exacting conditions between KCN and $CrCl_2$ or $CrCl_3$ respectively. They decompose quickly in air and often undergo a variety of additional reactions in solution. No uses were identified by Udy or in any of the literature investigated in preparing for this Profile Report. A maker or supplier of chromium cyanides could not be found and no process or industry could be identified which might produce chromium cyanides as a waste from any process. The presence of chromic cyanide was described by one source as a highly unlikely occurrence since cyanides can only exist in an alkaline media which would ordinarily precipitate trivalent chromium.[1981] No physical properties were found in any of the standard works that are consulted in these studies and identified in other Profile Reports.

2. TOXICOLOGY

Trivalent chromium compounds are said to be less toxic than the hexavalent chromium compounds. Eczema-like skin conditions from trivalent chromium contact have been reported.[0766] The toxicology literature discusses the hexavalent compounds in considerable detail but the available literature does not distinctly describe the hazardous properties of the trivalent compounds by themselves. The Threshold Limit Value (TLV) for trivalent chrome compounds is 0.5 mg per cubic meter.[0225] Internally, chrome salts act as an irritant causing tissue corrosion in the gastrointestinal tract. Complaints of a bad taste in the mouth, vomiting and bloody stools are often noted. In addition, the central nervous system is often involved and dilated pupils, coma, collapse, slow respirations, shock and death sometimes occur.[2028]

When drinking water contains fluoride in relatively low concentrations, it will help prevent dental caries. No ill effects will result from these small amounts of fluoride. Excessive fluoride which is ingested by drinking water with high fluoride content or ingesting other fluoride contaminated materials will produce an objectionable dental fluorosis accompanied by an embrittlement of bones. The fluorosis in bones can have a crippling effect when 20 or more milligrams of fluoride from all sources is consumed per day for 20 or more years. Death will occur when 2.2 to 4.5 grams of fluoride is consumed in a single dose.[1752]

Other Hazards

No other flammability or explosive hazards have been found to exist for these compounds.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The toxicity of the trivalent chrome compounds necessitates the use of careful precautions when storing, handling, transporting, disposing, or reusing these materials. Dried, waste chromic sulfate can be packed in multi-wall moisture resistant paper bags and in fiber drums.[2055] Chromic fluoride is shipped by Allied Chemical in 100- and 300-lb steel drums and it is believed that these are also adequate for the transportation of chromic fluoride wastes.[1980] The International Air Transport Association (IATA) classifies solid chromic fluoride as "other restricted articles"; Class B; no label is required. Chromic fluoride solutions are classified by the IATA as corrosive liquids, requiring a White Label. These materials should be stored in areas separate from food stuffs. The use of outer protective clothing, rubber gloves, and dust controlling breathing equipment is recommended for personnel handling open containers of this material to prevent the possibility of burns and skin lesions.

All personnel and supervisory staff that deal with these types of compounds should be well instructed in the precautions that must be undertaken to prevent hazardous exposure to these materials. These same precautions are, of course, applicable to any procedures or waste management techniques designed to reprocess, repurify, or reconcentrate these materials for reuse in the future.

Disposal/Reuse

Chromic sulfate and chromic fluoride do not occur in concentrated waste forms so that the chromium values could be more readily recovered. For the safe disposal of the trivalent chromium compounds, the acceptable criteria for their release into the environment are defined in terms of the following recommended provisional limits:

Contaminant In Air	Provisional Limit	Basis for Recommendation
Chromic sulfate	0.005 mg/M^3 as Cr	0.01 TLV
Chromic fluoride	0.005 mg/M^3 as Cr	0.01 TLV
Chromic cyanide	0.005 mg/M^3 as Cr	0.01 TLV

Contaminant In Water and Soil	Provisional Limit	Basis for Recommendation
Chromic sulfate	0.05 ppm (mg/l) as Cr	Drinking water standard
Chromic fluoride	0.05 ppm (mg/l) as Cr	Drinking water standard
Chromic cyanide	0.01 ppm (mg/l) as CN	Drinking water standard

Option No. 1 - Precipitation by pH Adjustment

Soda ash or other alkaline chemicals are added to trivalent chrome or other heavy metal solutions to adjust the pH to about 9.5;thereby precipitating the insoluble heavy metal hydroxide gels. Aluminum sulfate (alum) or other suitable flocculating agents are also often used to aid in precipitation, settling of the gels and clarification of the effluent. Slaked lime must also be added to precipitate insoluble calcium fluoride, a reaction which requires at least 24 hours. The effluent is neutralized before sewering and the resultant sludge is landfilled.[0095] The procedure can be carried out in either batch or continuous processes. Complete equipment systems are available for performing the precipitation on an automated or semiautomated basis. The biggest drawback of this procedure is the removal and disposal of the highly hydrated metal hydroxide sludges. It is not unusual for these sludges to contain upwards of 75 to 80 percent water by volume. Precipitation and settling is normally a slow procedure and with a high volume of effluent it is normally necessary to have settling ponds or lagoons in which to allow the slow coagulation process to function. The clear effluent can be removed and the residual sludge dried. No feasible economic process has yet been developed for the reclamation of valuable metals or other credits from this type of sludge since it often contains other organic and inorganic materials which hinders effective purification and recovery.

Three ultimate disposal options for these sludges are: (1) landfill, (2) incineration, and (3) ocean disposal. Landfill is believed to be, by far, the most prevalent final disposal procedure but the problem of potential contamination of surrounding land or water tables due to the leaching of poisonous materials from the sludge must be considered. It is therefore recommended that California Class 1 type landfill be utilized for these wastes. Incineration reduces the sludge to an ash residue which can be more easily handled for ultimate disposal but at the same time could also lead to the formation of poisonous soluble metal oxides. Incineration of course requires additional equipment and a combustible fuel source as well as equipment for air pollution control. Ocean disposal is currently being practiced to a considerable degree by municipal waste treatment plants located near the coast where the primary and secondary sludges can be either pumped or barged out to submarine disposal areas. This disposal approach has been the subject of much recent debate and it is likely that it will not long remain one of the significant sludge disposal options. These three sludge disposal options are discussed in greater detail in the Profile Reports on the chromate (ammonium chromate [21]) and dichromate (potassium dichromate [345]) salts.

Option No. 2 - Dilute Chrome Discharge to Municipal Sewers

The textile and leather tanning industries, the areas of nearly all the consumption of the subject hazardous materials, can both be characterized as relying mainly on municipal sewage treatment systems to handle the greatest proportion of their waste products in dilute effluents.[1601,0087,1988,1990,1991]

When discharged to sewers, most trivalent chrome will be precipitated in the sewers by sulfides found in the normal types of domestic and industrial sewage. Precipitation of chromic sulfide occurs in transit to the waste treatment plant and these solids are removed by the primary sedimentation and screening facilities of the water treatment plant.

It is currently feasible to treat tannery wastes including the chrome content in adequately designed and operated municipal waste water treatment plants where screening, flotation, and neutralization or precipitation are necessary pretreatments. This option is environmentally acceptable only when it is possible to construct adequate facilities in step with the demand on them.

To summarize, precipitation by pH adjustment is an adequate waste management method for trivalent chromium wastes; diluted discharge to municipal sewers can be considered adequate if municipal treatment facilities can efficiently remove the waste trivalent chromium. Whether the trivalent chromium is handled in a pH adjustment process or is precipitated as a result of sewering, the end result is a sludge of metal hydroxides or sewage solids containing precipitated chromium compounds. As discussed previously, the ultimate disposal of solids from public and private waste treatment still remains a difficult and critical problem. Again, it is recommended that Class 1 type landfill be utilized where significant levels of toxic metals are present in the sludges.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is recommended that processes for treating concentrated metal wastes be included in the design of National Disposal Sites but not necessarily for the compounds discussed in the Profile Report. The waste handling characteristics of the tanning and textile industries that create these waste materials are such that no waste stream segregation is being performed to capture these materials in concentrated form for transport to a National Disposal Site. In addition, the procedures currently being used either in the on-site industrial treatment plants and the municipal water treatment plants can be designed to adequately manage the chromic sulfate and chromic fluoride waste discharges as they are believed to currently exist. The facility that is recommended for a National Disposal Site should be used for various metal-containing, concentrated wastes which could occasionally need treatment. These would include other Cr compounds, Pb, Hg, Cu, and others.

It is, of course, necessary for those with authority in private and municipal waste water treatment to keep pace with the demands that these waste chromium compounds and other waste materials place upon the waste treatment plants. It is also reiterated that the greatest problem facing the current types of waste treatment previously discussed is that of disposing the solids and sludge material from the various and private municipal treatment plants.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chromic fluoride (485)

IUC Name

Common Names Chromium trifluoride

Structural Formula

CrF_3(1)

Molecular Wt. 108.99(1)

Melting Pt. 1000 C(1)

Boiling Pt. sublimes(1) (1100-1200)

Density (Condensed) 3.8(1) @

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble*

Hot Water

Ethanol insoluble

Others: slightly soluble acids; soluble HF and HCl

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification

IATA Classification Other resricted no label(as solid)

Comments 1) inorganic fluorides generally toxic and emit toxic fumes on heating,
2) or acid contact

*$CrF_3 \cdot 4H_2O$:S = 44.8% at 25C; soluble in hot water(1)

$CrF_3 \cdot 3H_2O$:S = 2.63% at 25C; 3.46% in hot water(1)

References (1) 1570
(2) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chromic Sulfate (486)

IUC Name

Common Names Chromium Sulfate, Wool Mordant

Structural Formula

$Cr_2(SO_4)_3$ (1)

Molecular Wt. 392.18(1) Melting Pt. Boiling Pt.

Density (Condensed) 3.012(1) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Both soluble and insoluble* Hot Water Ethanol slightly soluble

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments *Some chromic salts exist in two forms, a soluble and an insoluble modification Basic chromic sulfates existing varying mixtures and no one set of physical data is representative of the class of compounds.

References (1) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chromium Cyanide (487)

IUC Name

Common Names

Structural Formula

$Cr(CN)_2$ or $Cr(CN)_3$

Molecular Wt. Melting Pt. Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Hot Water Ethanol

Others:

Acid, Base Properties

Highly Reactive with Decomposes in air.

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments $CrCl_3 + 3KCN$ $Cr(CN)_3$ (a green blue precipitate in excess KCN)(1)

$CrCl_2 + 2KCN$ $Cr(CN)_2$ (a white precipitate) (1)

References (1) 2055

PROFILE REPORT

Copper (275), Lead & Zinc (276) Mill Tailings

1. GENERAL

Processing

The mill tailings environmental problems stemming from the production of copper, lead and zinc have been grouped in this Profile Report since the major ores (all sulphides) of these materials are concentrated in a similar manner. Though vast quantities of finely ground wastes are produced, they are in themselves innocuous and it is only the leachate of contained minerals or the small quantities of flotation reagents which are contained which could constitute hazards.

Typically, the processes involved in the production of a concentrate of the mineral of interest and the attendant waste product (tailings) for copper, lead, zinc follow this pattern:

(1) Crushing
(2) Gravity Separation (Lead and Zinc)
(3) Grinding
(4) Flotation Separation

Crushing. Crushing[2486] is predominantly 3-stage, comprising almost universally a jaw or gyratory crusher as the primary stage, a cone crusher as the secondary machine, and rolls or short-head cone crushers as the third stage. Oversize material from each stage of crushing is normally separated by grizzlies or screens and recirculated.

Gravity Separation. "The coarsely disseminated ores of lead, lead-silver, and lead-zinc, with gangue of average specific gravity (2.6 to 2.8) yield important quantities of high-grade lead concentrate by gravity concentration on jigs and/or tables."[2486]

Grinding. The crushed ore is then ground to an average size sufficient to liberate the ore mineral from the gangue (35 to 48 mesh or as fine as necessary to free the minerals). As in the crushing stage, oversize material is recirculated. In order to obtain the required recoveries a

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large amount of the material must of necessity be ground much finer than the average.

Flotation. Taggart's Handbook of Mineral Dressing [2486] describes flotation as a method of concentrating minerals in a relatively finely divided state. It is essentially a method of gravity concentration in water in which the effective specific gravity of the ore minerals is substantially decreased by causing air bubbles to attach to particles of the particular mineral of interest whereupon they float on the separating medium while the unaffected minerals (tailings) sink.

After grinding, the steps in froth flotation are: (1) dilution to a pulp consistency of 15 to 35 percent solids; (2) addition to the pulp of small quantities of conditioning agents, (burned lime or sulphuric acid for pH adjustment-1 to 4 lbs/ton, sodium cyanide, etc. .2 to 2 lbs/ton of ore), which prepare the mineral surfaces; (3) addition of a collector reagent which has the function of coating the mineral to be floated with a water repellant film (xanthates are commonly used for Cu, Pb and Zn-0.04 to 0.2 lbs/ton of ore); (4) addition of a frothing agent which imparts persistence to bubbles when they reach the surface (pine oils, eucalyptus oil, alcohols, etc. --0.4 to 0.1 lbs/ton of ore); (5) aeration by agitation or by air injection of a combination of the two; (6) separation of the mineral bearing froth from the liquid pulp containing the residual pulp.

Ores and Concentrates

Copper. As described in Taggart's Handbook of Mineral Dressing [2486] the primary sulfide economic minerals of copper are bornite [$Cu_5 Fe S_4$], Chalcocite [Cu_2S], Chalcopyrite [$Cu Fe S_2$], or native copper [Cu]. Copper is found in practically every type of ore deposit and associated, in one place or another, with practically every metallic and rock-forming mineral. The largest and best known deposits are the sulfide-vein deposits of Montana, the native-copper deposits of the Lake Superior region, and the "oxidized" and "porphyry" deposits of the southwestern United States. At Butte, Montana, the ore-bearing veins occur in granite, the chief copper minerals are chalcocite, enargite [Cu_3 (As, Sb) S_4], bornite, and chalcopyrite, and the principal associated vein minerals are quartz and pyrite. In the Lake Superior region the native copper, associated with native silver, occurs as part of the cementing matter in a conglomerate, as a cavity filling in lava beds, and in veins cutting both igneous and sedimentary rocks. The usual gangue minerals are calcite and zeolites. The "oxidized" deposits of the southwest carry amounts of the oxidized copper minerals, malachite, azurite, and cuprite, and directly below or closely associated with these, bonanzas of massive secondary chalcocite. Both classes of minerals are derived from the primary copper sulphides, largely chalcopyrite and cupriferous pyrite, which are found unaltered in greater depths. The deposits occur in limestone or at limestone-porphyry contacts. The "porphyry coppers" are mineralized zones in granitic porphyries and schists. The principal copper mineral is chalcocite, which occurs as grains and veinlets in the country rock. Pyrite, chalcopyrite, and magnetite are the principal metallic associates; quartz and the rock-forming silicates form the nomentallic gangue.

Copper ores may contain native copper (one mine operating in the United States) or either of the three sulphides, chalcocite, bornite or chalcopyrite, as the principal value-bearing constituent; in which case a given weight of copper-bearing mineral will carry respectively 100, 80, 56, or 35 parts of copper per 100 parts of pure concentrate, with a corresponding limitation on the highest possible grade of concentrate that can be made.

Most of the U.S. production (over 90%)^{1975} is presently derived from five western states. Most of the remainder comes from Michigan and Tennessee. Fifteen of the leading mines are located in Arizona, which produces more than 50 percent of the U.S. production. Arizona produces approximately 100 million tons of copper mill tailings per year. Utah ranks second with over 30 million tons of tailings per year. Mines and concentration plants in Michigan, Montana, Nevada, New Mexico and Tennessee make up the remainder.

Since most of the large disseminated ore bodies which are the primary source of present production range from 015 to 1.0 percent copper, the tremendous amounts of material which must be processed to produce concentrates approaching the theoretical limits required for the production of 1,205,000 tons of copper can easily be seen. Some typical analyses of copper tailings are shown in Table 1.[0169]

Lead & Zinc. "Occasionally one of these metals[2486] is found in economic quantities in an ore in which the other is lacking or is but a minor constituent; such occurrence is, however, so rare that the localities can almost be counted on the fingers of one hand, e.g., lead in southeastern Missouri, Leadville, Colorado, and Tintic, Utah, and zinc at Mascot, Tennessee, Franklin Furnace, New Jersey, and southwestern Wisconsin. The usual ores contain galena [PbS], and sphalerite [ZnS]; many carry important amounts of silver; minor amounts of copper are not uncommon and are usually accompanied by minor quantities of gold; pyrite and pyrrhotite are common associates; carbonates and quartz are the most usual rock-forming gangue minerals, but other gangue associates are legion.

The economic minerals of lead are galena [PbS], cerussite [$PbCO_3$], anglesite [$PbSO_4$], and pyromophite [$3Pb_3(PO_4)_2 \cdot Pb\ Cl_2$]. Galena ores comprise the great majority. There are three general classes: (1) those containing lead alone as an economic metal; (2) lead-zinc ores; (3) lead-silver ores.

Calcite, dolomite, and pyrite are the common gangue minerals of the first two classes, quartz of the third class.

The economic minerals of zinc are sphalerite, smithsonite, [$ZnCO$], calamine [$ZnSiO_3 \cdot Zn\ (OH)_2$], franklinite [$Zn\ Fe_2\ O_4$], willemite, and zincite. These are several distinct types of ores. Argentiferous and auriferous zinc sulphides with or without some lead, copper, and iron sulphides in quartzose gangue are typical of the Rocky Mountain deposits. Sphalerite alone or with galena and, usually, with some pyrite in limestone are typical of the Mississippi Valley deposits."

TABLE I

CHEMICAL ANALYSES OF COPPER TAILINGS

Location	SiO_2	Al_2O_3	Na_2O	K_2O	MgO	CaO	Cu	Fe	Ni	S	CO_2	TiO_2
Magna, Utah	70.8	12.0	1.0	5.1	3.9	1.7	0.10	2.7	0.002	0.95	0.23	0.35
Hayden, Arizona	81.33	8.50	0.4	4.0	0.86	0.14	0.115	3.75	---	--	--	.5
San Manuel, Arizona	67.2	13.3	1.5	6.0	1.5	1.28	0.06	2.4	---	1.00	--	0.8

Primary lead-zinc production, mostly from the state of Missouri, amounts to over 5.5 million tons per year, which leaves a residue of over 5 million tons per year of tailings. Tennessee represents the primary source of zinc in the United States with over 20 percent of the national production. Again, the production of 5.5 million tons of ore leads to a residue of over 5 million tons of tailings.

Though an average analysis for all lead mining operations, considering the varying geology of the areas of production, would not be meaningful, analyses typical of Missouri lead mines are shown below:[0169]

Old "Lead Belt"	-	52% $CaCO_3$, 40% $MgCO_3$
Joplin District	-	Predominantly Silica
New "Lead Belt"	-	52% $CaCO_3$, 40% $MgCO_3$

Plus Trace Impurities from Flotation and
Residual Lead and Zinc

A fairly typical analysis of tailings from zinc mines in Tennessee is shown as follows:[0169]

Chemical Analysis

SiO_2	R_2O_3	ZnS	$CaCO_3$	$MgCO_3$
9.80	1.45	0.18	52.30	36.35

Lime equivalent = 95.55

Screen Analysis

Screen Size	Wt % on Screen
+20	0.4
+35	8.0
+65	22.4
+100	11.0
+150	10.8
+200	6.0
-200	41.4
Total	100.0

2. TOXICOLOGY

Copper, lead and zinc tailings constitute a negligible toxicological hazard.

3. OTHER HAZARDS

The tailings, although not presenting a toxicological problem, constitute an environmental problem on the basis of three major elements: (1) the sheer volume of the refuse materials; (2) the dust problems encountered because of the fineness of tailings; (3) the production of acidic, iron containing leachates which may also contain small quantities of flotation reagents.

As an example of the types of leachates which may be produced, mine drainage (similar to the leachate produced from the tailings dumps) from a lead-zinc mine in southeast Kansas contained 1,000 ppm of iron at a pH of 2.65.[2485]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Present methods of waste management have evolved around the entrapment of the tailings in ponds and the subsequent stabilization of the dried tailings. As described in the Dames and Moore Engineering Bulletin No. 34, tailing ponds are developed by two basic methods:

"1) Building Retaining Dams.[2484] For this system, earth dams are constructed for retaining the tailings to the planned height. After the dams are completed, the tailings are deposited behind the dams in essentially the same manner as would be used to fill a water reservoir. Such dams are usually designed and constructed to water retention standards."

"2) Build With Tailings. Another system consists of building the dams by using the tailings themselves. A small starter dike is constructed with imported materials on the downstream side of the pond after that, the remaining perimeter embankments are constructed by controlling the hydraulic deposition of the tailings. Such control usually involved adjustments in the decant system of the pond and the use of a limited amount of imported fill. In developing ponds by this system, the various factors influencing water handling and embankment construction must be considered during the entire life of the tailings pond."

"The first system--involving the initial construction of earthen retaining dikes--usually results in a high initial investment but low operating costs. The second system--building with tailings--results in a low initial investment, but requires continuing attention during the operation of the facility. Most installations evolve into a combination of the two systems, particularly since the continuous desposition of tailings often requires a larger storage capacity than that available behind the initially constructed retaining dam."

Stabilization of tailings is presently being attempted by one, or combinations of the following methods:

1) Coatings. Some dried tailings areas have been covered with asphaltic or clay coatings to prevent the problems of blowing dust.

2) Chemical Stabilization.[0136] "Chemical stabilization involves reacting mineral wastes with a reagent to form a water- and air-resistant crust or layer. Many reagents have been tested on different tailings. These studies indicated that cement, lime, sodium silicate with $FeSO_4$ and $CaCl_2$ additives, oxidized pyrite or pyrrhotite, various lignin sulfonates, redwood bark extracts, amines, dicalcium silicate, bituminous base products, elastomeric polymers, sulfonated petroleum products, and resinous adhesives were effective stabilizers for most types of tailing wastes."

3) Vegetative Stabilization. Vegetative stabilization consists of providing a vegetative cover that renews itself and provides a suitable habitat for the enroachment of native plant species. This is normally accomplished by planting a mixture of seeds and seedlings native to the area of interest.

Though vegetative stabilization is the most ecologically satisfactory method of stabilization, it is complicated by the fact that most tailings are:[0136] "(1) deficient in certain plant nutrients; (2) unfavorable for plant growth due to textural and structural properties which adversely influence soil aeration and moisture; (3) include unconsolidated sands which, when windblown, tend to sandblast or bury young plants; (4) are light in color and reflect solar radiation to the darker surfaces of plants thus intensifying physiological stresses; (5) contain salts and heavy metal phytotoxicants that adversely affect plant growth."

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The disposal of tailings in ponds and subsequent stabilization by the methods described in Section 4 of this report are judged to be adequate methods of disposal.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is apparent that copper, lead and zinc tailings are not "hazardous" materials in a toxicological sense, though they are a large environmental problem, and consequently they are not candidates for National Disposal Sites.

However, it is readily apparent that much must be accomplished to make existing and future tailings ecologically acceptable. In the reduction of the environmental problems associated with tailings disposal, the following elements should be considered for research and development as well as the agronomical efforts required for the development of effective vegetative cover at each site. (1) A very inexpensive method of agglomerating tailings is required, both to improve the aeration characteristics of the soil and to improve its tilth; (2) less expensive means of chemically stabilizing tailings while vegetative stabilization is developing would be most useful; (3) one reference[0136] speaks of the advantages of adding sewage sludge to "improve the structure and add organic matter." Many municipalities are in difficult straits in their efforts to dispose of sewage sludge in a non-polluting manner. The development of an integrated system of sludge disposal and tailings stabilization could be most beneficial in many cases in aiding both mining companies and municipalities in solving their environmental problems.

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PROFILE REPORT

Slag I (SIC 3331) Copper Smelting (371) and Slag II (SIC 3332) Lead Smelting (372)

1. GENERAL

Introduction

Copper is extracted from ore concentrates by smelting in a reverberatory furnace. The materials may be prepared by drying or roasting or they may be charged directly into the furnace.

The molten charge in the furnace separates into layers of matte and slag. Slag is removed at this point while the molten matte is transferred to converters where silica flux is added and air blown through. Iron sulfide is oxidized and the iron is removed as a silicate slag, while the copper sulfide is converted to blister copper for further refining.

Lead sulfides are converted to oxides of lead and sulfur in the preliminary sintering step. The oxidized material is then reduced in the blast furnace to form impure metal and slag. To form the slag the materials used are limestone, silica, and small amounts of scrap iron. These are added in the amounts required to form a free running slag.

Composition

Copper. The two molten products of the reverberatory furnace generally have the following range of values (in percent):[2493]

Component	Matte	Slag
Copper	25-50	0.4-0.7
Iron	29-35	34 -40
Silica	0.8-1.0	35 -40
Sulfur	22-29	1.0-1.5

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Lead. The slag is removed from the blast furnace separately and is conveyed to a fuming furnace for recovery of lead and zinc. As it goes to the fuming furnace the slag contains 10 to 20 percent zinc, one to two percent lead, the remainder is mainly siliceous and contains iron and calcium.

Minor Constituents in Nonferrous Smelting. "Ores and concentrates of copper, zinc, and lead have varying amounts of minor constituents that sometimes require the use of special processing methods to recover them or to overcome or avoid the problems they could cause. There is not only considerable variation in the constituents from one smelter to another, but also from time to time in particular smelters. These constituents include chlorine compounds in lead smelters, fluorine in copper, zinc, and lead smelters, and arsenic in most ores of the western United States. Cadmium is commonly associated with zinc, and the quantities are large enough so that most plants recover it. Mercury is found in some zinc ores and has been recovered in some instances. Bismuth, selenium and tellurium are often present in ores of most nonferrous metals.

Volatile constituents such as arsenic get into the gases and usually deposit in the flue system. One copper smelter has recovered and purified arsenic for sale as a byproduct."[2943]

2. TOXICOLOGY

The leachates from slag dumps may present toxicological hazards depending upon the minor constituent metals contained in the slag of interest. The toxicological hazard and the recommended methods of treatment are discussed in the Profile Reports covering the metals of interest. Detailed chemical analysis of slags and leachates from each operation would be required to make a judgement since the feed ore and byproduct recovery are so variable.

3. OTHER PROBLEMS

Slags constitute an environmental problem mainly because of the large volume of material produced and the large amount of acreage utilized for their deposit.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Slag is generally dumped in the most economical, available area. Some efforts have been made to utilize slags as aggregates in concrete, for road metal etc., but the economic limits for the transportation of these low value products only allows them to be used in the area of the smelters.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Current disposal methods, as presented in Section 4 above are judged to be acceptable methods of slag disposal.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Because of their volume and their low toxicological impact, slags are not candidates for National Disposal Sites. To alleviate their environmental impact research efforts should be encouraged which will: 1) provide economical extraction of all metal values and 2) improve their acceptability to State Highway Departments and others for use as aggregate and other building products.

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PROFILE REPORT

Hydrazoic Acid (528)

1. GENERAL

Hydrazoic acid is a colorless liquid, of sharp, irritating odor with a boiling point of about 37 C. It is highly poisonous with a toxicity about equal to that of hydrogen cyanide. Liquid hydrazoic acid is very dangerous to handle owing to the ease with which it explodes.

Hydrazoic acid is a weak acid. It reacts with zinc, iron, magnesium, and aluminum to form azides with evolution of hydrogen. A small amount of ammonia is also produced, due to the reduction of hydrazoic acid. Hydrazoic acid also reacts with copper, silver and mercury to form azides without loss of hydrogen. A considerable amount of hydrazoic acid is reduced to ammonia of hydrazine and free nitrogen in these systems. Hydrazoic acid, like nitric acid, oxidizes hydrogen sulfide to form sulfur:

$$HN_3 + H_2S \rightarrow S + N_2 + NH_3$$

When mixed with hydrochloric acid it forms a solution resembling nitrohydrochloric acid in its properties and is capable of dissolving noble metals.

There are two methods for the manufacture of hydrazoic acid or its salts. One is based on the action of nitrous acid on hydrazine:

$$N_2H_4 + HNO_2 \rightarrow HN_3 + 2H_2O$$

An excess of nitrous acid decomposes hydrazoic acid in accordance with the equation as follows:

$$HN_3 + HNO_2 \rightarrow N_2 + N_2O + H_2O$$

This is a quantitative reaction and is used to destroy waste azides.

Nitrous esters may be employed for the manufacture of hydrazoic acid, e.g., ethyl nitrate in the presence of sodium hydroxide.

$$N_2H_4 + C_2H_5NO_2 + NaOH \rightarrow NaN_3 + C_2H_5OH + 2H_2O$$

With this reaction sodium azide is formed instead of hydrazoic acid. The second method of manufacture is based on the action of nitrous oxide on sodium amide.[1662,2171]

Hydrazoic acid is not normally sold or shipped even in laboratory quantities.[1411] In the laboratory, sodium azide is reacted with sulfuric acid and the resultant hydrazoic acid purified by distillation.[2171]

The physical/chemical properties of hydrazoic acid are summarized in the attached worksheet.

2. TOXICOLOGY

Vapors of hydrazoic acid irritate the respiratory tract, particularly the nasal mucosa, and its aqueous solution burns the skin. Hydrazoic acid interferes with the oxidation-reduction processes in the human body causing injury to kidneys and spleen. Headache, weakness, and unsteadiness have also been reported following continued industrial exposure. The chief physiological effect of azides is a marked lowering of the blood pressure with an accompanying rise in heart beat and an increase in respiration rate. Concentrations in air within the range 0.5 to 7.0 mg/M^3 evoke marked symptoms of intoxication. The toxic effect may be delayed; symptoms appearing the day following exposure.[2171] A Threshold Limit Value (TLV) for hydrazoic acid has not been established by the American Conference of Government Industrial Hygienists.[0225]

3. OTHER HAZARDS

Liquid hydrazoic acid explodes on heating to 100 C in a tube. An explosion may also occur on rapid cooling or on handling the liquid under vacuum or in passing compressed oxygen into a vessel containing liquid hydrazoic acid. In dilute aqueous solution hydrazoic acid is stable and not liable to decompose even on long boiling. However, a 17 percent aqueous solution of hydrazoic acid can detonate. Gaseous hydrazoic acid is liable to non-explosive decomposition above 250 C. At 33 C its half-life is 12 min. Hydrazoic acid decomposes when exposed to ultraviolet light.

The heavy metal azides are used as primary explosives, and are extremely sensitive to mechanical, electrical or thermal shock. For this reason, extreme caution should be employed in handling HN_3 which has been in contact with heavy metals. The acid should be handled in all-glass equipment.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Hydrazoic acid in aqueous solution dissolves iron, zinc and copper with formation of the azide, nitrogen and ammonia, but glass equipment is satisfactory for handling hydrazoic acid. When required as acid rather than as one of its salts, the hydrazoic acid is usually prepared at the location where it is to be used.[2171] No commercial source for hydrazoic acid exists, and there are no regulations permitting its shipment.

The safe disposal of hydrazoic acid is defined in terms of the recommended provisional limits in the atmosphere and in water and soil. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Hydrazoic acid	0.005 mg/M^3	0.01 of minimum level that produces symptoms of in intoxication.[2171]

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Hydrazoic acid	0.025 mg/l	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Hydrazoic acid as a waste will not be encountered in large quantities and a satisfactory method for its destruction exists. An excess of nitrous acid decomposes hydrazoic acid in accordance with the following equation:

$$HN_3 + HNO_2 \rightarrow N_2 + N_2O + H_2O$$

This reaction is accomplished by diluting the hydrazoic acid with 500 times its weight of water, slowly adding 12 times its weight of a 25 percent solution of sodium nitrite, agitating, and then slowly adding 14 times its weight of a 36 percent solution of nitric acid or glacial acetic acid. A red color produced on addition of ferric chloride solution indicates azide to be present; more time or additional reagents are required to effect complete destruction of azide.[1147,2169] After pH adjustment to 6.0 to 9.0, the reacted solution is diluted to a nitrite and nitrate concentration of less than 450 ppm, a typical maximum allowable concentration in an effluent being discharged to a storm sewer or stream.[0536]

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The difficulty encountered in shipping hydrazoic acid and the limited quantity used indicates that it is not a likely candidate waste stream constituent for a National Disposal Site. The treatment facilities that will be available at a National Disposal Site will permit easy treatment of hydrazoic acid, if ever required. The only facilities required are for diluting, addition of chemicals, and mixing.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Hydrazoic Acid (528)

IUC Name Hydrazoic Acid

Common Names Azoimide

Structural Formula

NH_3

Molecular Wt. 43.03   Melting Pt. -80 C   Boiling Pt. 37 C

Density (Condensed) @   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water 2.14 ml/100 ml   Hot Water 0.85 ml/100 ml   Ethanol 6.925 gm/100 ml

Others:

Acid, Base Properties Weak acid, $K = 2.8 \times 10^{-5}$

Highly Reactive with reducing agents, iron, zinc, copper

Compatible with hydrocarbons, glass

Shipped in not normally shipped

ICC Classification   Coast Guard Classification

Comments

References (1) 1416

PROFILE REPORT

Hydrobromic Acid (Hydrogen Bromide) (213)

1. GENERAL

Hydrogen bromide is a colorless, very irritating, corrosive gas at atmospheric temperature and pressure. As a liquid, it has a yellow color. In cylinders, hydrogen bromide is a liquified gas at 70 F with a vapor pressure of about 320 psig. HBr is very soluble in water; hydrobromic acid is sold commercially as a 47 to 49 percent solution of HBr in water. Hydrogen bromide adds to olefins and acetylenes, and is used as a catalyst in a variety of organic reactions. Hydrobromic acid is used for the preparation of numerous inorganic bromides.

Hydrogen bromide is obtained as a by-product of the substitution bromination of organic compounds.[1140] The physical/chemical properties of hydrogen bromide are summarized in the attached worksheet.

2. TOXICOLOGY

Hydrogen bromide, like hydrogen chloride, is a toxic gas. It is severely irritating to the upper respiratory tract and corrosive to the eyes, skin and mucous membranes. The recommended maximum allowable concentration for an 8-hr exposure is the 5 ppm Threshold Limit Value (TLV). Because of its irritation to the upper respiratory tract, hydrogen bromide provides adequate warning for prompt voluntary withdrawal from contaminated atmospheres.

Contact of the eyes with hydrogen bromide gas rapidly causes severe irritation of the eyes and eyelids. Hydrogen bromide has a corrosive action upon the skin and mucous membranes. It will cause severe burns.

When hydrobromic acid in a waste stream is neutralized with sodium hydroxide or carbonate, the stream will contain sodium bromide. Since bromide ion is intermediate in abundance between chloride and fluoride in natural waters, the presence of small additional concentrations of bromide over that already present should present no problem. The total amount of bromine in the earth is estimated at 10^{16} tons of which about half is thought to be contained in living organisms. Sea water contains 50 to 65 ppm of bromide. The presence of some bromide is necessary for plant and mammal metabolism.[1140] Limits for bromide concentration in streams and lakes have not been established, but waste streams that do not cause an elevation of the bromide content of natural streams and lakes above 50 ppm should generally be acceptable. Evidence that small quantities of bromide do not affect humans is demonstrated by the fact that as much as 0.45 g of sodium bromide administered daily to tuberculomeningitic patients increased the blood bromide level to 5 to 10 times normal. This level was maintained for several months without any serious side effects.[1140]

3. OTHER HAZARDS

Hydrogen bromide is resistant to oxidation. The dry gas is essentially non-reactive with commonly used structural metals under normal conditions (room temperature and one atmosphere of pressure). In the presence of moisture, hydrogen bromide will corrode most metals other than silver, platinum, and tantalum.[1301]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

Adequate procedures for the safe handling, transportation and storage of hydrogen bromide are provided by Matheson Company, Inc.[1301] Their Gas Data book provides recommended procedures for equipment design, leak tests, first aid, employee safety, and material specifications. The handling of aqueous solutions of hydrogen bromide (hydrobromic acid) is similar to that of any strong acid.

Hydrogen bromide is classified by Department of Transportation (DOT) as a nonflammable gas and is shipped in cylinders under a Green Label. Hydrobromic acid (HBr solution in water) is shipped in glass bottles and carboys as a corrosive liquid under a White Label.

Disposal Reuse

Hydrogen bromide as gas, as solute in organic solvents, and as hydrobromic acid in water solution is not normally discharged as a waste, but is recovered because of its economic value.

In those instances in which discharge is necessary, the safe disposal of hydrogen bromide is defined in terms of the recommended provisional limits in the atmosphere and in water and soil environments. These provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
HBr	0.03 ppm	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis Recommendation
HBr	0.50 ppm	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

In most industrial processes where hydrogen bromide or hydrobromic acid are evolved as by-products, the recovery of hydrogen bromide is essential for the commercial viability of the process. Impure hydrogen bromide or hydrobromic acid usually can be sold to bromine and hydrogen bromide manufacturers. Hydrobromic acid is often converted to bromine by the chlorination process[1305] (see Profile Report on Bromine [65]).

Hydrogen bromide gas is purified by cooling to -60 C to freeze out any moisture and most of the solvent vapors present. The partially purified hydrogen bromide is then solidified with liquid air or nitrogen. Fractionation permits the recovery of pure hydrogen bromide. The methods described briefly above are in commercial use and are satisfactory for recovery of HBr.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

With the exception of the return to the manufacturers of contaminated hydrobromic acid (hydrogen bromide) or hydrobromic acid converted to impure bromine, hydrobromic acid (hydrogen bromide) waste streams can be best handled at the site where they are created by regeneration of purified hydrogen bromide or preparation of bromine. Designated sites (located at Br_2 or HBr manufacturers) should be identified for processing and purification of impure hydrogen bromide or bromine for resale.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Hydrogen Bromide (213)

IUC Name Hydrogen Bromide

Common Names Anhydrous hydrobromic acid

Structural Formula

HBr

Molecular Wt. 80.92   Melting Pt. -87 C   Boiling Pt. -67 C

Density (Condensed) 2.16 g/ml. @ -67 C   Density (gas) 3.64 g/L @ 0 C (STP)

Vapor Pressure (recommended 55 C and 20 C)

320 psig @ 70 F   114 psig @ 0 F   Crit. Temp. @ 91 C

Flash Point ______   Autoignition Temp. ____

Flammability Limits in Air (wt %)   Lower NA   Upper NA

Explosive Limits in Air (wt. %)   Lower NA   Upper NA

Solubility

Cold Water 70 g/100g   Hot Water -   Ethanol -

Others: Acetic acid @ 11 C - 41% (w/w)

Acid, Base Properties Apparent dissociation in 0.1 N soln. at 20°C = 93%

Highly Reactive with all bases

Compatible with most metals when dry. In presence of moisture, compatible with Ni, Au, Ta, and stainless steel.

Shipped in steel cylinders, as liquified gas

ICC Classification White label, non-flammable   Coast Guard Classification Non-flammable gas, green label

Comments

Constant boiling mixture with water, 47%, has b.p. of 126 C

References (1) 1140

PROFILE REPORT

Hydrocyanic Acid (215) and Hydrogen Cyanide (218)

1. GENERAL

Hydrogen cyanide (also known as hydrocyanic acid) is a water-white liquid at temperatures below 26.5 C. It has a faint odor of bitter almonds. Hydrogen cyanide is miscible in all proportions with water and alcohol, and in aqueous solution is weakly acidic; dissociation constant at 18 C is 1.3×10^{-9}. When not stabilized, hydrogen cyanide polymerizes spontaneously with explosive violence. Hydrogen cyanide is manufactured commercially by six different processes: (1) by treating a cyanide, usually sodium or calcium, with dilute sulfuric acid; (2) by catalytically reacting ammonia and air with methane or natural gas; (3) by recovery from coke oven gases; (4) decomposition of formamide; (5) from ammonia and hydrocarbons by electrofluid reaction in the presence of a platinum-rhodium catalyst; and (6) by pyrolytic decomposition of residues from beet-sugar molasses. The principal uses of hydrogen cyanide are in the manufacture of acrylonitrile, acrylates, adiponitrile, cyanide salts, dyes, fumigants, chelates, rubbers, and plastics.[1433]

The physical/chemical properties for hydrogen cyanide are summarized in the attached worksheet.

2. TOXICOLOGY

Human Toxicity

Hydrogen cyanide and the cyanides are true protoplasmic poisons, combining in the tissues with the enzymes associated with cellular oxidation. They thereby render the oxygen unavailable to the tissues, and cause death through asphyxia. The suspension of tissue oxidation lasts only while the cyanide is present; upon its removal, normal function is restored provided death has not already occurred. Hydrogen cyanide does not combine easily with hemoglobin but does combine easily with methemoglobin to form cyanmethemoglobin. Exposure to concentrations of 100 to 200 ppm for periods of 30 to 60 min can cause death. The Threshold Limit Value (TLV), American Conference of Governmental Industrial Hygienists (ACGIH) recommended, is 10 ppm in air (11 mg per cubic meter). Hydrocyanic acid can be absorbed through the skin.[0536]

Other Toxicity

Cyanides, either as hydrogen cyanide or its salts, are important industrial chemicals, and because of their solubility in water are often found in industrial aqueous waste streams. At low pH values, cyanide, as hydrocyanic acid, is especially toxic. Cyanide ion is, for the most part, unaffected by the basic water treatment plant. Many lower animals and fish are able to convert cyanide to thiocyanate ion, which does not inhibit respiratory enzyme activity. Hence, a permissible criterion has been recommended of 0.20 mg/l for waste discharged into streams, and a desirable criterion of complete absence from public waters was recommended by the Federal Water Pollution Control Administration (FWPCA) Water Quality Committee.[0536]

3. OTHER HAZARDS

When hydrogen cyanide is exposed to heat, flame or oxidizing chemicals, a fire or explosion may occur. Under certain conditions, particularly contact with alkaline materials, hydrogen cyanide can polymerize or decompose explosively. The compressed gas is commonly stabilized by addition of acids.[1416]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Liquid hydrogen cyanide is subject to the Department of Transportation (DOT) regulations for the transportation of explosives and other dangerous articles. It is defined a Class "A" poison. The commercial product usually contains 96 percent to 98 percent hydrogen cyanide with the balance water and small quantities of free mineral acids (about 0.05 percent) for stabilizing purposes.

When hydrogen cyanide is stored in bulk, steel storage tanks are used that should be kept cool and protected from mechanical injury. Routine inspection for stability (liquid colorless) should be carried out. Before filling with hydrogen cyanide, containers should be cleaned and treated to remove alkaline contaminants.

Hydrogen cyanide is packed for interstate shipment in metal cylinders, which must have not more than 125-lb water capacity and must be charged with not more than 0.6 lb of liquid for 1-lb water capacity of the cylinder. Before shipment, the cylinder must be tested to insure against leakage. This is done by passing a piece of paper treated with sodium picrate over the closure to test for escape of hydrogen cyanide. The cylinder must carry a "Poison Gas" label. Shipment may be made by freight but is not accepted by Railway Express.[1433]

Disposal/Reuse

Hydrogen cyanide appears in both aqueous and gaseous waste streams from hydrogen cyanide manufacturing plants, acidified cyanide salt (plating shops, metal treating plants, etc.), organic chemical and plastic manufacturing, and fumigating operations. In addition, coal coking and degassification plants and oil refining operations produce hydrogen cyanide as one of the byproducts. Complete removal of hydrogen cyanide from the effluent is difficult. HCN passes into waste water in the course of the wet scrubbing processes used to remove the H_2S, NH_3 and phenol contaminants. Alkaline scrubbing usually converts most of the hydrogen cyanide to the alkaline cyanide salt. Hydrogen and the residual unstripped hydrogen cyanide, though sometimes vented, are usually sent to a furnace where they are used as a fuel.[1963] Provisional limits for public exposure resulting from the disposal of hydrogen cyanide have been defined in this study. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
HCN	0.11 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
HCN	0.01 mg/l as CN	Drinking Water Standard

The quantities and locations of wastes containing HCN are too diverse to summarize, since HCN is normally discharged as a very dilute solution.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Hydrogen cyanide in aqueous streams is easily destroyed by first adjusting the pH to the 10 to 11 range and adding chlorine or hypochlorite which converts the cyanide to cyanate. Then the pH is adjusted to the 8 to 9 range and further oxidizing agent converts the cyanate to carbon dioxide and ammonia. Other methods though not often used are available and are discussed in the combined Profile Report for the cyanide salts. In an alternate equally acceptable method, hydrogen cyanide is removed from aqueous solution by passing air through the solution. The venting of this air containing hydrogen cyanide is not recommended, but instead the contaminated air must be passed through an alkaline scrubber.

The destruction of hydrogen cyanide is usually accomplished by incineration which produces only carbon dioxide and nitrogen along with possibly some NO_x that can be stripped from the incinerator effluent with an alkaline scrubber,[1562] or reduced over a catalyst.

Air containing hydrogen cyanide, either as an effluent from a storage tank, process, or from stripping of an aqueous solution, is absorbed by passing the air through a sodium or potassium hydroxide scrubber which produces the cyanide salt. The salts obtained in this manner are recovered upon evaporation of the water.[1963]

The disposal processes described are equally acceptable. The selection of disposal processes are governed by the economics of destruction/recovery.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Hydrogen cyanide does not appear to be a candidate waste stream constituent for National Disposal Sites. It is anticipated that aqueous a and gaseous waste streams containing hydrogen cyanide will continue to be treated at the source of the waste generation.

7. REFERENCES

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1562. Graham, A. K. Electroplating engineering handbook. 2d ed. Westwood, New York, Metals and Plastics Publications Inc., 1962. 774 p.

1963. Kaumert, P. Hydrogen cyanide recovery. U. S. Patent 3,096,156. May 1963.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Hydrogen Cyanide (218)

IUC Name Hydrogen Cyanide

Common Names Hydrocyanic Acid, Prussic Acid

Structural Formula

HCN

Molecular Wt. 27.03   Melting Pt. -13.2 C   Boiling Pt. 25.7 C

Density (Condensed) 0.688 @ 20 C   Density (gas) 0.969 @ 31 C

Vapor Pressure (recommended 55 C and 20 C)

360 torr @ 7 C   658.7 torr @ 21.9 C   @

Flash Point 0 F   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water miscible   Hot Water miscible   Ethanol miscible

Others: ether-miscible

Acid, Base Properties Acid, weak

Highly Reactive with must be stabilized with acids, reacts with bases

Compatible with most metals

Shipped in metal cylinders, 125-lb water capacity

ICC Classification Class "A" Poison   Coast Guard Classification Class "A" Poison

Comments Critical temperature 183.5 C

References (1) 1433

PROFILE REPORT

Hydrogen Sulfide (221)

1. GENERAL

Hydrogen sulfide is a toxic, flammable gas with a pungent odor, which appears in a number of chemical industry waste streams (in particular in refinery and natural gas processing waste streams). Approximately 1 million tons per year of elemental sulfur are recovered from hydrogen sulfide waste streams in the refinery industry alone. At least an equal amount of waste hydrogen sulfide is burned and vented to the atmosphere as sulfur dioxide. A detailed discussion on the fate of hydrogen sulfide in refinery operations is presented.[0742] Physical/chemical properties are summarized in the attached worksheet.

2. TOXICOLOGY

Human Toxicity

Hydrogen sulfide is a highly toxic gas which is extremely dangerous in very low concentrations. The Threshold Limit Value (TLV) for hydrogen sulfide is 10 ppm as defined by the American Conference of Governmental Industrial Hygienists (ACGIH). This represents the condition to which nearly all workers may be repeatedly exposed, day after day, without adverse effect. H_2S is both an irritant and an asphyxiant and may be characterized by its repugnant odor of "rotten eggs." The toxic hazard is aggravated because unprotected exposure to nontoxic levels of hydrogen sulfide results in temporary olfactory fatigue limiting the capability to detect dangerous levels. Human toxic effect as a function of time and concentration is outlined (Table 1).

TABLE 1

ACUTE EFFECTS OF HYDROGEN SULFIDE GAS[0743]

Concentration (ppm)	Time	Effect
0.13	Sniff	Odor detectable
10.0	8 hours	Threshold limit
50-100	1 hour	Mucous membrane irritation
200-300	1 hour	Mucous membrane irritation (severe)
500-700	1/2 hour	Coma
900	Minutes	May be fatal
1000	Minutes	Fatal

The acute effects of hydrogen sulfide inhalation represent the most serious threat in handling. Although it is not a cumulative poison, severe exposure may result in brain damage from oxygen deficiency if breathing is not rapidly regained. Permanent olfactory damage (loss of sense of smell) may result from extended exposure at less than lethal levels.

Exposures in the 700 to 1,000 ppm range may be fatal in 30 minutes. Very high concentrations will be instantly fatal.

Toxicity Towards Aquatic Life

The toxicity of inorganic sulfides (primarily H_2S) to fish increases as the pH value is lowered. However, inorganic sulfides have proved fatal to sensitive fish, such as trout, at concentrations between 0.5 and 1.0 mg/l even in neutral and somewhat alkaline solution.[0091] Sulfides impart an unpleasant tase and odor to drinking water at concentrations as low as 0.2 mg/l.[0091]

3. OTHER HAZARDS

Hydrogen sulfide is an extremely flammable gas. It burns in air to form sulfur dioxide and water with the liberation of heat. In concentrations of 4.3 to 46 percent H_2S by volume in air it explodes upon ignition. A mixture of (2) volumes of hydrogen sulfide and (3) of oxygen explodes violently upon ignition. The autoignition temperature of hydrogen sulfide is 500 F. This very low autoignition temperature indicates the relative ease with which hydrogen sulfide/air mixtures can be inadvertently ignited. Open flames, hot surfaces, and sparks will ignite combustible or explosive H_2S/air mixtures. Because of the extremely high vapor pressure of liquid hydrogen sulfide, contact with the skin will result in severe frostbite.

4. DEFINITION OF WASTE MANAGEMENT PRACTICES

Handling, Storage, and Transportation

Adequate procedures for the safe handling, storage, and transportation of concentrated hydrogen sulfide wastes are described in detail by Stauffer Chemical Company,[0743] and the Manufacturing Chemists Association.[0744] These documents provide recommended procedures for building design, equipment design, ventilation, air analysis, electrical equipment design, employee safety, design of shipping and storage containers, federal classification and regulations, tank and equipment cleaning and repairs, emergency rescue, first aid, and material specifications.

H_2S is classified by the Department of Transportation (DOT) as a Flammable Compressed Gas with a maximum permitted filling density of 62.5 percent in cylinders (Spec. 3A480, 3AA480, 3B480, 4A480, 4B480, 26-480, 3E1800) and 68 percent in tank cars (105A-600W). All federal labeling, loading, and handling regulations must be followed.

Disposal/Reuse

A definition of acceptable criteria for the disposal of hydrogen sulfide must also take into account acceptable criteria for the release of sulfur dioxide to the environment since current practice in hydrogen sulfide disposal usually involves processing the hydrogen sulfide to sulfur and/or sulfur dioxide. The acceptable criteria for the release of H_2S and SO_2 into the environment are defined in terms of the following recommended provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Hydrogen sulfide	0.1 ppm (0.15 mg/m^3)	0.01 TLV
Sulfur dioxide	0.05 ppm (0.13 mg/m^3)	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Hydrogen sulfide	0.75 ppm (mg/l)	Stokinger and Woodward Method
Sulfur dioxide	0.65 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Figure 1 summarizes H_2S disposal options for both sour (H_2S containing) gas streams and sour water streams. Current practice as well as processing options which are currently in pilot plant or demonstration plant stages of development are included. Typical or expected effluent concentrations of SO_2 and H_2S are indicated (Figure 1) for each of the processing options. The processing options are very briefly described in the following paragraphs together with recommendations as to adequacy. Detailed discussions of the major processing options are presented in the referenced waste treatment process reports.

Sour Gas Disposal Processes

Sour gas waste streams which provide the input feed to H_2S disposal processes may contain in addition to H_2S, hydrocarbons, carbon monoxide, carbon dioxide, nitrogen, and ammonia, and traces of other sulfur compounds and phenols.

Option No.1 - Incineration or Combustion in Heaters and Boilers. Current practice in some installations involves direct combustion of the H_2S in the sour gas waste stream and venting of the residual SO_2 gas directly to the atmosphere. This procedure is only adequate if the concentration of H_2S in the sour gas stream is very low and the throughput is small. In order to be adequate under current regulations the final effluent concentration of SO_2 in the stack must be less than 500 ppm and no more than 200 lb/hr of SO_2 must issue from a single stack.

Option No.2 - Removal of H_2S from Sour Process Streams by Amine Scrubbing.[0539,0360] Scrubbing solutions of monoethanolamine or diethanolamine in aqueous solution are very effective in removing H_2S from sour gas streams and this practice is used extensively in the refinery industry. H_2S can be removed from a gas stream by amine scrubbing down to a concentration level of a few parts per million. Regeneration of the rich amine solutions yields a stream of concentrated

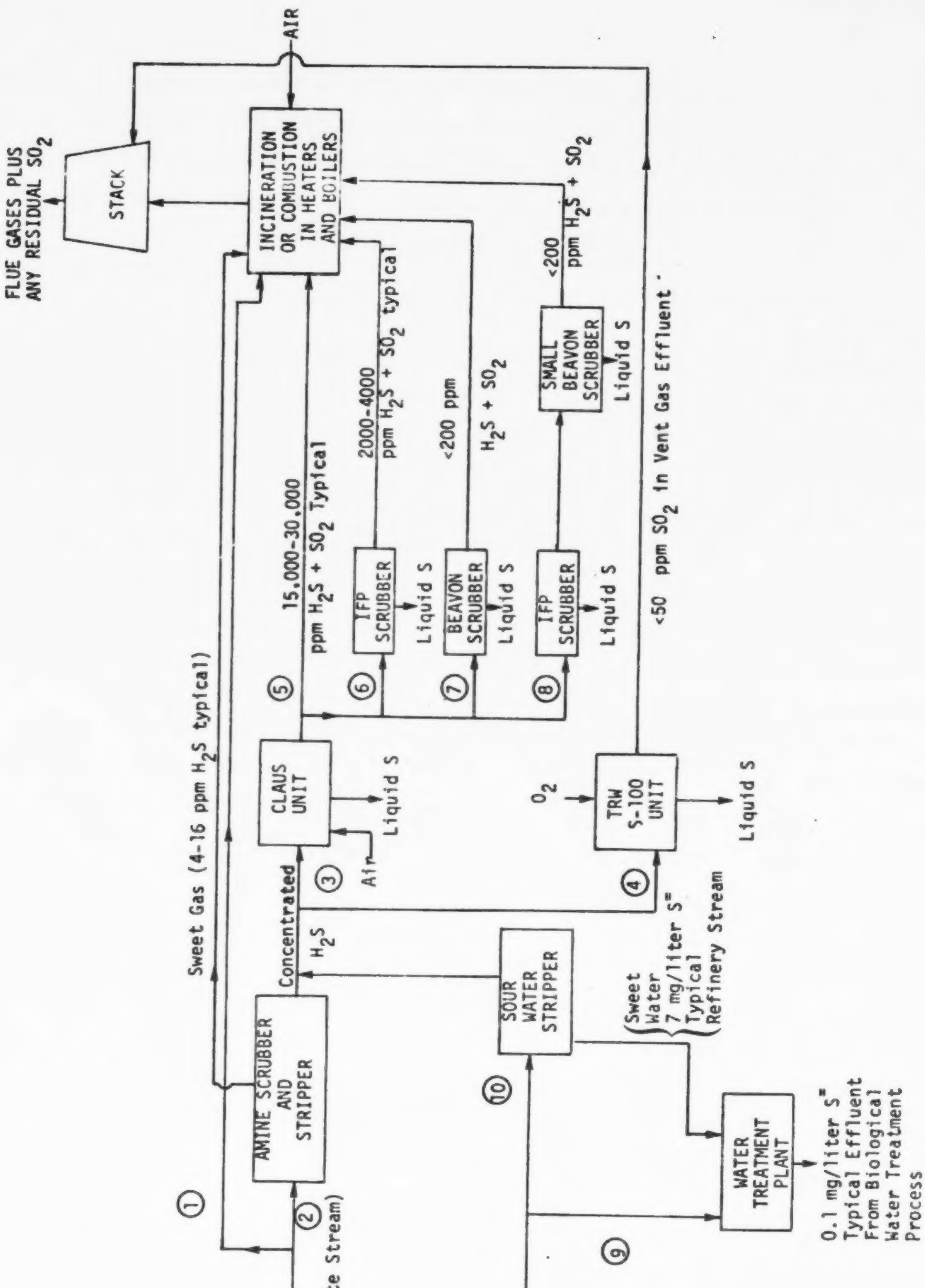
Sour Gas
(H$_2$S Waste Stream)
①
②
AMINE SCRUBBER AND STRIPPER
Sweet Gas (4-16 ppm H$_2$S typical)
Concentrated H$_2$S
③
Air
CLAUS UNIT
Liquid S
④
O$_2$
TRW S-100 UNIT
Liquid S
⑤
15,000-30,000 ppm H$_2$S + SO$_2$ Typical
⑥
IFP SCRUBBER
Liquid S
2000-4000 ppm H$_2$S + SO$_2$ typical
⑦
BEAVON SCRUBBER
Liquid S
<200 ppm H$_2$S + SO$_2$
⑧
IFP SCRUBBER
Liquid S
SMALL BEAVON SCRUBBER
Liquid S
<200 ppm H$_2$S + SO$_2$
<50 ppm SO$_2$ in Vent Gas Effluent
INCINERATION OR COMBUSTION IN HEATERS AND BOILERS
AIR
STACK
FLUE GASES PLUS ANY RESIDUAL SO$_2$
Sour Water
⑨
⑩
SOUR WATER STRIPPER
Sweet Water 7 mg/liter S$^=$ Typical Refinery Stream
WATER TREATMENT PLANT
0.1 mg/liter S$^=$ Typical Effluent From Biological Water Treatment Process

Figure 1. H$_2$S waste treatment process (Option tree).

H_2S (50-100 percent typical) which must either be recycled for reuse within the plant or further processed on a pollution-free basis to sulfur. Amine scrubbing units are considered to be adequate for removing all but the last few ppm of H_2S from process gas streams. It is normal to convert the residual few ppm of H_2S to SO_2 by combustion prior to venting the stream gas to the atmosphere.

Options No.3 and No.5 - Claus Process for Conversion of a Concentrated H_2S Stream to Elemental Sulfur.[0362] Claus process units are universally used in refineries and natural gas processing plants to convert a concentrated stream of H_2S (from regeneration of amine scrubbing solutions and from sour water stripping units) into high purity elemental sulfur which is sold as a product. Unfortunately, existing Claus systems are not adequate from a pollution viewpoint without modification in that they convert on the average only about 93 percent of the incoming H_2S stream into elemental sulfur. The remaining sulfur exits the process as a high concentration stream of H_2S + SO_2 which is usually combusted to yield a final effluent of 15,000 to 30,000 ppm of SO_2 which is vented to the atmosphere. As a result of this deficiency in the basic Claus process, several modifications (or "hang-on" units) have been developed to further treat the effluent from a standard Claus Unit to produce additional sulfur and less sulfur oxide pollutants.

Option No. 6 - Claus-IFP Process for Conversion of a Concentrated H_2S Stream to Elemental Sulfur.[0363] This process results in further treatment of the effluent from a standard Claus unit to yield more elemental sulfur and a final vented effluent concentration of SO_2 of 200 to 400 ppm. The effluent SO_2 concentration from this process is still too high to be considered adequate.

Option No.7 - Claus-Beavon Process for Conversion of a Concentrated H_2S Stream to Elemental Sulfur.[0367] The Beavon unit operates on the effluent gas from a Claus plant and results in additional conversion of H_2S + SO_2 to sulfur and a final vented effluent which is reported to contain less than 200 ppm SO_2.[0367] The Beavon system has been operated at the large pilot plant scale but has not yet been introduced on a commercial scale. If it performs as reported, the Claus-Beavon process is adequate for converting a concentrated H_2S stream to sulfur.

Option No.8 - Claus-IFP-Beavon Process for Conversion of a Concentrated H_2S Stream to Elemental Sulfur. This combination of a Claus, IFP, and small Beavon unit results in slightly lower capital and operating costs than the Claus-Beavon system. However, this sequence of unit operations has not yet been demonstrated. In principle it should have about the same operating characteristics as the Claus-Beavon system and hence should be adequate for treating concentrated waste H_2S streams.

Option No.4 - TRW S-100 Process for Conversion of H_2S Streams to Elemental Sulfur. Recently, TRW conceived a new process (designated S-100) for converting H_2S wastes to elemental sulfur. The great advantage of the TRW process over the current Claus system is that the TRW process S-100 is extremely efficient in recovering the sulfur and emits an exceedingly small quantity of sulfur compounds to the atmosphere. This new process has been investigated in bench and pilot-plant studies but has not as yet been demonstrated as a complete system on a commercial scale. The S-100 process shows promise of being a lower cost method of converting H_2S to sulfur on essentially a pollution-free basis as indicated below. S-100 processing details are presented in TRW's "Proposal for Demonstration of the TRW S-100 Process."0742

Process	Capital Cost $ Million	Effluent Purity ppm SO_2	Lbs of SO_2 Emitted to the Atmosphere Per Lb of H_2S Fed to the Process
S-100	1.2	<50	$<2 \times 10^{-5}$
Claus	0.9	15,000 - 30,000	5×10^{-2} to 2×10^{-1}
Claus + IFP	1.2	2,000 - 4,000	9×10^{-3} to 2×10^{-2}
Claus + Beavon	2.1	<250	$<1 \times 10^{-3}$
Claus + IFP + Beavon	2.0	<250	$<1 \times 10^{-3}$

Sour Water Disposal Process

In addition to waste gas stream containing H_2S, hydrogen sulfide may also appear as a dissolved gas in waste water streams (sour water streams) which are sent to municipal or industrial waste-water treatment plants.

Option No. 9 - Sour Water Stream is Sent Directly to Water Treatment Plant Without Pretreatment. This option is only adequate when the concentration of H_2S in the waste water is relatively low and the magnitude of the sour water stream is fairly small. Since biological treatment processes, such as activated sludge or aerated lagoon systems, only have a sulfide removal efficiency of 90 to 99 percent,[0091] the influent streams should contain no more than 1-10 mg/l of sulfide in order to insure that the effluent from a biological water treatment plant contains less than the recommended maximum of 0.1 mg/l of dissolved hydrogen sulfide. In addition, high concentrations of sulfides must be reduced in sour waters before biological treatment as they are toxic to the microorganisms present in the biological treatment units.

Option No.10 - Sour Water Stream is Processed in a Stripping Unit Prior to Discharge into the General Waste Water System for Biological Treatment. For sour water streams containing high concentrations of dissolved H_2S, the sour water can be stripped of H_2S with steam or flue gas in a packed or plate-type column.[0091] Hydrogen sulfide gas released from the waste water can be recovered as sulfur by one of the waste gas processing options discussed previously. The bottoms from the column have a low enough sulfide concentration to adequately permit discharge into the general waste water system for biological treatment. Sour water stripping units can be expected to achieve H_2S removal efficiencies of 85 to 99 percent.[0091]

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that systems to handle the great majority of the hydrogen sulfide waste streams generated in the chemical process industries will continue to be located at the source of H_2S waste generation rather than at National Disposal Sites in view of the economics involved. However, some capacity to process H_2S waste to sulfur on a pollution-free basis is required at National Disposal Sites to handle the following kinds of requirements:

(1) Occasional tank-cars or other smaller lots of extremely hazardous liquid hydrogen sulfide which for one reason or another are required to be disposed of in a safe, pollution-free manner.

(2) Secondary sour gas or sour water streams generated within the National Disposal Site as the result of processing other sulfur containing wastes.

(3) Regeneration of amine (H_2S) scrubbing solutions from refinery operations if the National Disposal Site is located within reasonable pipeline distance from the refineries.

It is suggested that the following kinds of unit operations will be required at National Disposal Sites:

(1) H_2S Scrubbing and Stripping Units

Ethanolamine scrubbing units are used in many refineries and are recommended for National Disposal sites for initial removal of H_2S from sour gas streams. The rich amine solutions are regenerated by heating and a concentrated stream of H_2S passes out of the stripping tower and is sent to the sulfur recovery plant.

(2) Sour Water Stripping Unit

A plate-type or packed column for initially stripping H_2S from sour waste waters with steam or flue gas will be required at National Disposal sites. The concentrated H_2S gas is sent to the sulfur recovery plant.

(3) Sulfur Recovery Plant

Sulfur recovery from concentrated H_2S streams must be performed on essentially a pollution free basis. The following processes are considered to be adequate:

Process	Order of Preference	Remarks
Claus-Beavon	First Choice	Demonstrated technology; adequate sulfur recovery
TRW S-100	Second Choice	Looks better on paper but not yet demonstrated
Claus-IFP-Beavon	Third Choice	Never been operated as a single plant so that projections of lower cost have not yet been demonstrated

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name HYDROGEN SULFIDE (221)

IUC Name HYDROGEN SULFIDE

Common Names SOUR GAS

Structural Formula

H_2S

Molecular Wt. 34.08 Melting Pt. -82.9°C Boiling Pt. -76.4 C (760 torr)

Density (Condensed) .790 gram/cc @ 60 F Density (gas) 34 g/liter @ 0 C and 1 atm p

Vapor Pressure (recommended 55 C and 20 C)

300 psia @ 75 F 80 psia @ 0 F 400 psia @ 100 F

Flash Point ______ Autoignition Temp. 260 C

Flammability Limits in Air (wt %) Lower 4.3% Upper 46%

Explosive Limits in Air (wt. %) Lower 4.3% Upper 46%

Solubility

Cold Water 430 cm^3/liter H_2O 0 C 1 atm H_2S pressure Hot Water 186 cm^3/liter H_2O 40 C 1 atm H_2S pressure Ethanol ______

Others: ______

Acid, Base Properties Weak Acid

Highly Reactive with Strong oxidizers, nitric acid, attacks many metals forming sulfides, extremely flammable

Compatible with 316 stainless steel, superalloys, some low carbon steels-do not use copper or brass tubing or fittings

Shipped in Specially designed tank trailers and tank cars (1)

ICC Classification (2) Red label flammable compressed gas 0744 300 lbs max. Coast Guard Classification Inflammable gas red label

Comments Extremely hazardous material due to combination of toxicity, flammability, explosiveness, and usual storage under high pressure. (1),(2)

References (1) (0743)

(2) (0744)

PROFILE REPORT

Lead (233)

1. GENERAL

Lead is a soft, heavy, bluish-gray metal. Its surface oxidizes readily, and is then very resistant to corrosion. It is soluble in nitric acid and in many organic acids, but not in dilute sulfuric or hydrochloric acid, and is one of the most stable metals. Lead and its compounds are cumulative poisons and should not be used in contact with foods. It is used for containers and tank linings for many corrosive liquids, such as sulfuric acid. Lead as the metal and as the dioxide is used in large quantities in storage batteries. The metal and its alloys are used in solders, type metal, bearings, pipe, cable covering, plumbing, ammunition, and in the manufacture of tetraethyl- and tetramethyl lead. It is also used as a sound absorber and as a radiation shield.

Lead ores are usually sulfides (galena, PbS), oxides, or carbonates. By means of complicated flotation, leaching, and smelting processes, lead is recovered from its ores. Lead not recovered will generally end up in slag piles.[1433]

The chemical/physical properties of lead are summarized in the attached worksheet.

2. TOXICOLOGY

Lead is present in the individual's normal environment. The daily intake of lead in the food and beverage of American adults is about 0.3 mg. The human body is capable of eliminating this amount daily. However, if more lead is taken into the system than is eliminated, a condition exists which is referred to as "chronic lead poisoning."

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Initially, the symptons of lead intoxication usually take the form of weakness, pains in the joints, severe constipation, and colic-like pains. Exposure over longer periods of time will frequently intensify the pains in the joints and the weakness of the muscles. Acute attacks of colic will develop.[0766]

Lead may enter the human system through inhalation, ingestion, or skin contact. Industrially, inhalation of dust, mist, or fumes is the chief method by which lead and its inorganic compounds may enter the body. In practice, the amount of lead or its inorganic compounds in the work atmosphere should not exceed an average of 0.2 mg of lead per cubic meter for an 8-hr working day of a 40-hr work week, Threshold Limit Value (TLV). Ingestion is not an important form of lead exposure in the present-day industrial establishment when care is taken to avoid its contact with food.[1699] Direct skin contact is of negligible importance in connection with inorganic lead compounds. However, in the case of organic lead compounds, skin contact can be a real hazard.[0766]

The toxicity of lead and its inorganic compounds varies with several factors of a chemical and physical nature. The most important considerations are the form in which the lead is present, the particle size, and the length of exposure time. The fineness of the lead-containing particles is of great importance. Particles above 10μ are frequently not absorbed in the lungs at all and are screened out by the nasal mucosa and hairs. It is generally only particles below 5μ that are retained to any extent, and retention is at a maximum below 1μ. Plants handling lead must, therefore, take care to avoid creating fine lead particles; or if produced, personnel must be protected from fine dusts.[0766]

3. OTHER HAZARDS

Lead does not usually present any special hazards other than those associated with its toxicology.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Lead is insoluble in water and therefore, its use in pipes and as a joint dope is harmless with most water supplies. Some waters do dissolve lead from plumbing, but the reasons are not known. Naturally soft waters which are slightly acid and low in mineral content are the most corrosive and should not be used with lead plumbing. When lead compounds are used in ceramic glazes, lead is solubilized and extracted by the organic acids present in food and the use of lead compounds in glazes is therefore a serious hazard. A maximum level with respect to extractable lead in ceramic glazes is 7 mg per milliliter, released after extracting a piece of dinnerware for 24 hours at room temperature in a 4 percent acetic acid solution.[1699] Atmospheric lead contamination by discharge from (1) primary and secondary lead smelters, (2) combustion of coal and fuel, (3) incineration, and (4) combustion of gasoline containing lead antiknock additives is a serious health problem.[1699]

Lead is usually shipped as pigs or in fabricated form. There are no special regulations governing the transportation of lead.

The safe disposal of lead is defined in terms of the recommended provisional limits in the atmosphere, and in water and soil. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis of Recommendation
Lead	0.0015 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis of Recommendation
Lead	0.05 ppm	Drinking Water Standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Recent estimates indicate that 42 percent of all lead is reclaimed with the remainder continuing in use or lost in dumps or to the environment in an uncontrolled manner. The chief sources of reclaimed scrap include automobile storage batteries, cable sheathing, plumbing pipes, sheets, solder, joint caulking, type metal, freight car bearings, loaded brass and bronzes, spent ammunition, discarded ballast, foil, and blast furnace matte. Reclamation and processing of scrap are less costly sources of lead metal than mining and smelting primary lead, and replaces primary lead production to the extent available. Processes for reclaiming lead from scrap or blast furnace matte are briefly discussed in the following paragraphs together with recommendations as to adequacy.

Current Processes

Option No. 1 - Melting into Ingots. If scrap lead is pure, it is melted and cast into ingots for sale and shipment.[1699] The off-gas from furnaces used to melt lead is cooled by air dilution and then filtered by a cloth bag dust collector used in conjunction with other dust collecting equipment such as a cyclone.[0635, 0673] The particulate matter is then returned to the furnace. When the scrap is pure or nearly pure lead, this is obviously the recovery method of choice.

Option No. 2 - Recovery in Lead Blast Furnace. Blast furnaces used for smelting lead ore are also used for the secondary recovery of lead from such sources as battery plates. In a blast furnace, scrap lead to be recovered along with a mixture of roasted and part unroasted ore is charged to the furnace with iron oxide, silica and carbon. Upon heating, the copper present collects in the iron sulfide matte (which also contains 0 to 18 percent lead) while other metals remain in the lead. In refinement of the crude blast furnace lead, the more electropositive impurities are removed by air oxidation from frequent stirring of the molten lead over a several hour period. The impurities, when oxidized, rise to the surface and are skimmed off. Off-gas from smelting plants is cooled by air dilution and then filtered by a cloth bag dust collector used in conjunction with other dust collecting equipment such as a cyclone.[0635,0673] The particulate matter is then returned to the smelter. If the lead contains appreciable quantities of bismuth, the lead is purified electrolytically.[1326] These custom smelting plants provide the most efficient and economical means for the recovery of lead. For efficient operation, a smelting plant requires a continuous supply of raw materials which can best be supplied with a mixture of primary and secondary lead. Also, a smelting plant requires a large capital expenditure which can only be justified by a large continuous operation. The use of smelters is recommended because more than 80 percent of the secondary lead is recovered by this means.[1326]

Option No. 3 - Recovery from Blast Furnace Matte. A process developed by the Bureau of Mines at the College Park Metallurgic Research Center recovers lead and copper from lead matte.[0128] In this process, all the sulfides are first oxidized to sulfates by roasting, so that subsequent water leaching of the roasted products will extract the copper and other water-soluble salts. The copper is recovered from solution by cementing with iron powder. The water-insoluble residue is treated with a saturated brine solution to dissolve lead as a lead chloride complex while the associated sulfate ion is rendered insoluble by formation of calcium sulfate upon treatment with lime. The dissolved lead is then precipitated as $3\ PbO \cdot PbCl_2$ by the addition of more lime. An alternate method that does not require roasting involves oxidation by the bacterium Ferrobacillus ferrooxidans in dilute sulfuric acid solution or by air oxidation of a dilute sulfuric acid leach. The lead and copper sulfates are recovered as described above. The lead oxide is reduced by treatment at high temperature with carbon or carbon monoxide.

Option No. 4 - Assignment to Land Fills. Because lead is insoluble in water and not attacked by most inorganic acids or bases, lead in small quantities is often disposed of in landfills.[0095] Though this disposal method is satisfactory under most conditions, it is not recommended because lead is lost to future use. In addition, under certain conditions, lead is solubilized as either the chloride or the sulfate, which are both slightly soluble in water.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Lead present in most waste forms or lead alloys can best be recovered by returning the lead-containing wastes to blast furnaces designed for processing primary lead. Numerous companies purchase or salvage scrap lead which is then sold to primary lead processors.[1326] Therefore, processes for the recovery of lead are not a candidate for National Disposal Sites.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead (233)

IUC Name Lead

Common Names Plumbum

Structural Formula

Pb

Molecular Wt. 207.21 Melting Pt. 327.43 C Boiling Pt. 1740 C

Density (Condensed) 11.3437g/cc @ 20 C Density (gas) - @

Vapor Pressure (recommended 55 C and 20 C)

1.0 torr @ 987 C 10 torr @ 1167 C 100 torr @ 1417 C

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble Hot Water insoluble Ethanol insoluble

Others: soluble-nitric acid, most organic acids

Acid, Base Properties

Highly Reactive with most organic acids in presence of oxygen.

Compatible with most inorganic acids and bases except nitric acid.

Shipped in pigs

ICC Classification none Coast Guard Classification none

Comments

References (1) 1433

PROFILE REPORT ON LEAD COMPOUNDS

Lead Acetate (234), Lead Carbonate (237)
Lead Chlorite (238), Lead Nitrate (240), Lead Nitrite (241)

1. GENERAL

Introduction

In spite of its position in Group IVA of the periodic table, the usual valence of lead in its compounds is +2 instead of +4. In many properties the bivalent lead compounds resemble those of some of the alkaline earth elements such as barium and strontium. They also show a remarkable tendency toward forming basic salts of both anhydrous and hydrated types. Lead forms a soluble acetate, nitrate, nitrite, a slightly soluble chlorite, and an insoluble carbonate.

Among the five lead salts covered in this report, the chlorite and nitrite are not known to have any significant commercial and industrial consumption as reflected by the fact that no producer or distributor of these two compounds in the United States is listed in the major references of chemical suppliers.[1571,1670,1790] Consequently, the emphasis of this Profile Report will be placed on the acetate, carbonate, and nitrate. However, any pertinent information for the chlorite and nitrite are included wherever they were available.

Lead Acetate

Lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, is also known as plumbous acetate or sugar of lead. It is a colorless monoclinic crystal or white granules or powder. It is poisonous.[1492] It is manufactured by dissolving litharge (PbO) in hot dilute aqueous acetic acid solution.[2272] On cooling, large crystals are formed and can be separated by filtration. Its uses are:

(1) manufacture of other lead salts as basic lead carbonate and lead chromate;

(2) as a mordant in dyes;

(3) as a drier in paints;

(4) lead-coating of metals;

(5) as an analytical reagent;

(6) as an astringent on unbroken skin and mucous membranes;

(7) as an astringent and sedative on bruises and superficial inflammatory conditions for animals;

(8) formerly used internally as an astringent for diarrhea and in form of rectal suppositories for hemorroids.

Lead Carbonate

Normal lead carbonate, $PbCO_3$, occurs naturally as the mineral cerussite. It is a white to grayish ore found in conjunction with other lead minerals, being formed by the action of carbonated water on galena (lead sulfide) or its oxidation products. In the pure state, it is a colorless crystal or rhombic form. It is practically insoluble in water. It has a limited use in the paint and ceramic industries. More important commercially, and manufacturered in larger tonnage, however, is the basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$, also known as the white lead.[1433] It is a heavy, white powder, insoluble in water and alcohol.

White lead is formed when various basic salts of lead are treated with CO_2. Commercially, metallic lead or litharge, PbO, is used.[2273] CO_2 gas is passed through an aqueous solution of litharge in the presence of a small quantity of acetic acid. A series of chemical reactions is believed to take place as follows.[2275] First, litharge is hydrolyzed to form lead hydroxide which reacts with acetic acid to form normal (or neutral) lead acetate. The latter dissolves additional lead hydroxide to yield basic lead acetate. Finally, CO_2 reacts with basic lead acetate to yield basic lead carbonate and reproduce normal lead acetate. The basic lead carbonate formed is precipitated and separated from the solution by filtration. The filtrate is recycled to digest more litharge. So, the acetic acid plays the role of catalytic agent in the cycle with normal lead acetate acting as a solvent for lead hydroxide.

White lead has been one of major pigments in making white paint. However, due to its poisoning effect, particularly to small children, its use in house paint is an environmental issue and its future is somewhat uncertain. Basic lead carbonate is also used in cements, in making putty and lead carbonate paper, and in the processing of parchment.[1492]

Lead Nitrate

Lead nitrate, $Pb(NO_3)_2$, forms colorless cubic or monoclinic columnar crystals. It is highly soluble in water and poisonous.[1492] It is manufactured by reacting litharge (PbO) or metallic lead, or lead carbonate with nitric acid.[2274] Its uses are:[1492]

(1) manufacture of matches and special explosives;
(2) as a mordant in dyeing and printing on textiles;
(3) manufacture of other lead salts;
(4) as a mordant for staining mother-of-pearl, horn;
(5) as an oxidizer in dyes industry;
(6) as sensitizer in photography;
(7) process engraving;
(8) as a chemical reagent;
(9) formerly, as an astringent and antiseptic for external use.

Other Lead Compounds

Very little information is available regarding the properties, manufacturing methods, and uses for lead chlorite and nitrite. Pertinent data available are presented as follows:[0766,1433,1492]

Lead chlorite, $Pb(ClO_2)_2$, is a yellow crystal of monoclinic form. It is slightly soluble in water. Upon heating to 126 C, it explodes. Hence, it causes a severe explosion hazard when exposed to heat. Lead nitrite, $3PbO \cdot N_2O_3 \cdot H_2O$, is a light yellow powder or crystal. It is a powerful oxidizing agent, thus a potential fire and explosion hazard, however, the details of such hazards are unknown. It is also listed as poisonous.[1492] Large amounts taken by mouth may produce nausea, vomiting, cyanosis, collapse and coma.

Sources and Types of Wastes

The only significant wastes containing the lead compounds under consideration in this report have been found to come from the following sources: (1) paint manufacturers; (2) printing ink manufacturers; and (3) paint residue left in old containers.

In the manufacture of solvent-based paints, sludges are generated from both the washing system and the solvent recovery stills. The combined solvent-based paint sludge is characterized by the following composition: 4.5 percent inorganic pigment (excluding titanium dioxide), 8.5 percent titanium dioxide, 14.5 percent pigment extenders, 25.0 percent binders and 47.5 percent organic solvents. It is estimated that a total of 49,700 lb of lead carbonate are lost through 37 million lb of solvent-based paint sludges every year.*

Lead pigments are still used by some manufacturers in the production of certain types of printing inks and wastes are generated as a result of the operations to clean up the ball mills, mixing tanks, and other equipments. The typical liquid waste may contain 300 to 1000 ppm of lead (mostly as lead carbonate) mixed with varying amounts of other metals in organic solvents and water washes. It is estimated that a total of 21,000 lb of lead are lost through 2.1 million lb of liquid wastes per year.†

The lead carbonate containing paint residues left in containers normally discarded in municipal dumps constitute another source of lead carbonate wastes. It is estimated that a total of 344,000 lb of lead carbonate are lost as paint residues every year.‡

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*†‡The basis for these estimates are discussed in detail in the appendix volume on Waste Forms and Quantities.

Physical and Chemical Properties

The physical and chemical properties of five lead salts are given in the attached worksheets.

2. TOXICOLOGY

All of the lead compounds are sufficiently soluble in digestive juices to be considered toxic.[1433] In general, lead poisoning may be caused by (1) inhalation of dusts, fumes or vapors; (2) ingestion of lead compounds; and (3) absorption through the skin. However, there is no evidence that inorganic lead compounds can be absorbed through the skin in sufficient quantities to produce lead intoxication.[1433]

Lead is a cumulative poison.[0766] Increasing amounts of lead could build up in the body and eventually a point is reached where symptoms and disability occur. The symptoms of lead poisoning may be classified according to their clinical picture as: (1) aliminetary; (2) neuromotor; and (3) encephalic.

The alimentary type occurs most frequently. It is characterized by abdominal discomfort or pain. Other complaints are constipation and/or diarrhea, loss of appetite, metallic taste, nausea and vomiting, lassitude, insomnia, joint and muscular pains, irritability, headache and dizziness. In the neuromuscular type, the chief complaint is weakness, frequently of the extensor muscles of the wrist and hand, unilateral or bilateral. Gastroenteric symptoms are usually present, but not as severe as in the alimentary type of poisoning. Lead encephalopathy is the most severe but the rarest manifestation of lead poisoning. It may be caused by rapid and heavy lead absorption. Lead encephalopathy begins abruptly, and is characterized by signs of cerebral and meningeal involvement. There is usually stupor, progressing to coma, with or without convulsion, and often terminates in death.

For treatment of lead poisoning, it has been found that the chelating agent, calcium ethylenediaminetetracetate (CaEDTA), and related compounds are highly efficacious in removing absorbed lead from the tissues of the body. CaEDTA is effective only when administered intravenously.

Of the various lead compounds, the carbonate, monoxide, and sulfates are considered to be more toxic than metallic lead or other lead compounds. The Threshold Limit Value (TLV) for lead in air recommended by the American Conference of Governmental Industrial Hygienists, 1971, is 0.15 mg/M^3. The lethal doses reported for the lead compounds are given below:[1312]

(1) Lead acetate:

iv LD_{50}	120 mg/kg, rat
ip LD_{50}	150 mg/kg, rat

(2) Lead carbonate (neutral):

ip LD_{CA}	124 mg/kg, guinea pig

Lead carbonate (basic):

MLD, orally	1.0 g/kg, guinea pig

(3) Lead nitrate

ip LD_{CA}	270 mg/kg, rat

(4) Lead chlorite and Nitrite: No data

The U.S. Public Health Service has established the limits and ranges of lead concentrations in public water affecting human health as follows:[1752]

(1) Physiologically safe:

Lifetime	0.05 mg/l
Short period, a few weeks	2-4 mg/l

(2) Harmful range:

Borderline	2-4 mg/l for 3 months
Toxic	8-10mg/l for several weeks

Lethal	Unknown, but probably more than 15 mg/l for several weeks

Lead in soft water is highly toxic to certain fish; 0.1 mg/l is toxic to small sticklebacks, larger fish are somewhat less susceptible to lead poisoning.

For lead nitrate, there is an additional toxic effect. Serious and occasionally fatal poisonings in infants have occurred following ingestion of well waters shown to contain nitrate (NO_3^-). This has occurred with sufficient frequency and widespread geographic area to require an assigned limit to the concentration of nitrate in drinking water. The limit recommended by the U.S. Public Health Service is 10 mg nitrate nitrogen (or 45 mg nitrate) per liter of water.[1752]

3. OTHER HAZARDS

Lead nitrate is a powerful oxidizing agent. Fire hazard is moderate. It may also explode when shocked, exposed to heat or flame or by spontaneous chemical reaction.

Lead nitrite is also a powerful oxidizing agent. However, little is known about its details on fire and explosion hazards.

Lead chlorite causes a severe explosion hazard when exposed to heat.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Because of the hazard of lead poisoning, special care must be exercised in the handling, storage and transportation of all lead compounds. In storage, they should be kept in the original containers supplied by the manufacturers and away from feed and food products. Powerful oxidizing agents, such as lead nitrate and lead nitrite, should be kept away from materials which are either flammable or susceptible to oxidation easily. To prevent explosion caused by spontaneous chemical reaction, the nitrate, nitrite, and chlorite should be stored in cool and well-ventilated areas.

In handling the lead compounds, the most important thing is to avoid breathing any lead-containing dusts, fumes, or vapors. Therefore, the use of respiratory protective devices is recommended. In shipping, lead acetate is labeled as Class B poison and lead nitrate, as oxidizing material. They must be shipped in accordance with the U. S. Department of Transportation (DOT) or IATA regulations.

Disposal/Reuse

Contaminated lead compound wastes could be reprocessed. The main consideration is the economic feasibility. For the safe disposal of these compounds, the acceptable criteria for their release into the environment are defined in terms of the following recommended provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Lead Acetate	0.0015 mg/M^3 as Pb	.01 TLV
Lead Carbonate	0.0015 mg/M^3 as Pb	.01 TLV
Lead Chlorite	0.0015 mg/M^3 as Pb	.01 TLV
Lead Nitrate	0.0015 mg/M^3 as Pb	.01 TLV
Lead Nitrite	0.0015 mg/M^3 as Pb	.01 TLV

Contaminant in Water	Provisional Limit	Basis for Recommendation
Lead Acetate	0.05 ppm (mg/l) as Pb	Drinking Water Standard
Lead Carbonate	0.05 ppm (mg/l) as Pb	Drinking Water Standard
Lead Chlorite	0.05 ppm (mg/l) as Pb	Drinking Water Standard
Lead Nitrate	0.05 ppm (mg/l) as Pb	Drinking Water Standard
Lead Nitrite	0.05 ppm (mg/l) as Pb	Drinking Water Standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Dilute Waste

Option No. 1 - Sulfide Precipitation. Three of the lead compounds in this report, the acetate, nitrate, and nitrite are very soluble. Even for the less soluble lead chlorite, removal of lead from an aqueous waste stream by simple filtration is no longer satisfactory. The filtrate still contains too high a lead concentration. Therefore, it is necessary to convert them into an insoluble compound. The general practice is to convert the soluble lead salts into the insoluble lead sulfide using hydrogen sulfide.[2272] The lead sulfide precipitate is removed by filtration. For current industrial practice, the filtrate stream is discharged to a settling pond.[2273] Periodically, the deposit from the pond is removed and sent to a smelter for recovery of the lead content. The effluent from the pond can be safely discharged.

Option No. 2 - Carbonate Precipitation. Soluble lead salts can also be removed from aqueous waste streams as insoluble lead carbonate by the addition of ammonium carbonate. Since lead carbonate is scarcely soluble in water, it can be economically removed from water by simple filtration. For example, at 20 C, only 0.11 mg of normal lead carbonate dissolves in one liter of water. This is equivalent to 0.085 mg Pb/l and is not far above the recommended provisional limit of 0.05 mg Pb/l in water. The filtrate can be further treated as described in Option No. 1.

Concentrated Waste

Option No. 1 - Conversion to Sulfide. Contaminated solid wastes of lead compounds are generally treated with concentrated nitric acid to form the nitrate which is then converted to lead sulfide by hydrogen sulfide.[0095] The insoluble lead sulfide is removed by filtration and sent to a smelter to recover its lead content. The filtrate may be treated as described previously.

Option No. 2 - Landfill. Disposal of soluble lead compounds such as the acetate, nitrate and nitrite by landfill technique is generally unacceptable. Even the slightly soluble lead chlorite should not be disposed of by landfill. However, lead carbonate is practically insoluble in water and, in fact, occurs naturally as the mineral cerussite. Similiarily, lead sulfide is also insoluble in water and occurs naturally as the mineral galena. Therefore, disposal of these two lead compounds by the landfill technique in California Class I type disposal sites might be considered adequate.

In summary, soluble lead wastes in aqueous waste streams can be treated adequately by precipitation as the sulfide or as the carbonate. For lead containing solid wastes, conversion to either the sulfide or the carbonate and followed by either lead recovery in smelters or disposal in California Class I type landfills are considered adequate methods of management.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Since lead is toxic in nature and has inherent value as a raw material, it is a common practice for the lead compound manufacturers and users to recycle the waste streams and to recover the waste product. Furthermore, the precipitation methods for the removal of lead from spent aqueous reaction solutions is effective and inexpensive enough for all lead compound manufacturers or users to operate. The lead carbonate and lead sulfide sludge deposits from the settling ponds can be sent to smelters for the recovery of the lead value or can be adequately disposed of in California Class I type landfills. It is concluded that the disposal of lead wastes can be handled adequately at the industrial site level and does not warrant consideration for treatment at the National Disposal Site.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead Acetate (234)

IUC Name

Structural Formula

$Pb(C_2H_3O)_2 \cdot 3H_2O$

Common Names

Molecular Wt. 379.34 (1)   Melting Pt. 75 C (1)   Boiling Pt. decomposes @ 200 C

Density (Condensed) 2.55 @   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water 45.61 g/100 cc @ 15 C   Hot Water 200 g/100 cc @ 100 C   Ethanol insoluble

Others: soluble in glycerol

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification   Coast Guard Classification

Comments

References (1) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead Carbonate, basic (237)

IUC Name

Common Names

Structural Formula

$2PbCO_3 \cdot Pb(OH)_2$

Molecular Wt. 775.67 Melting Pt. decomposes @ 400 C Boiling Pt.

Density (Condensed) 6.14 @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble Hot Water insoluble Ethanol insoluble

Others: soluble in HNO_3

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead Chlorite (238)

IUC Name

Common Names

Structural Formula

$Pb(ClO_2)_2$

Molecular Wt. 342.09 Melting Pt. explodes @ 126 C Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.095 g/100 cc @ 20 C Hot Water 0.42 g/100 cc @ 100 C Ethanol

Others: soluble in KOH

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead Nitrate (240)

IUC Name

Common Names

Structural Formula

$Pb(NO_3)_2$

Molecular Wt. 331.20

Melting Pt. decomposes @ 470 C

Boiling Pt.

Density (Condensed) 4.53 @

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@

@

@

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 37.65 g/100 cc @ 0 C

Hot Water 127 g/100 @ 100 C

Ethanol 8.77 @ 22 C in 43% alcohol

Others: soluble in alkali, NH_3

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification

Coast Guard Classification

Comments

References (1) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead Nitrite (241)

IUC Name ______

Common Names ______

Structural Formula

$3PbO \cdot N_2O_3 \cdot H_2O$

Molecular Wt. 763.60 Melting Pt. ______ Boiling Pt. ______

Density (Condensed) ______ @ ______ Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

______ @ ______ ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water very soluble Hot Water ______ Ethanol ______

Others: soluble in dil HNO_3

Acid, Base Properties ______

Highly Reactive with ______

Compatible with ______

Shipped in ______

ICC Classification ______ Coast Guard Classification ______

Comments ______

References (1) 1570

PROFILE REPORT

Lead Oxides (242)

1. GENERAL

Introduction

Lead forms a number of oxides. There are the monoxide (PbO), the dioxide (PbO_2), the sesquioxide (Pb_2O_3), the tetroxide (Pb_3O_4), and the suboxide (Pb_2O). They are all insoluble in water. With the exception of the monoxide, they decompose upon heating to elevated temperatures and therefore possess no true melting point. Absorbed into the body, they cause the well-known lead poisoning. Since only the monoxide and the tetroxide are of industrial importance, the discussion in this report will be focused upon these two oxides.

Lead Monoxide[1433]

Lead monoxide, PbO, also called plumbous oxide, exists in two polymorphic forms; the tetragonal reddish crystal, α-PbO or litharge, and the orthorhombic yellow crystal, β-PbO or massicot. Commercially, litharge and tetraethyl lead are the two most important lead compounds. The lead monoxide is produced in large tonnage by many different processes to suit specific applications. Four major manufacturing processes based on furnace techniques are in use.

(1) Metallic lead is partially oxidized and milled to a powder (called the black oxide in trade) which is charged into a reverberatory furnace at about 600 C to complete the oxidation to yield the ordinary "chemical" litharge.

(2) Pig lead is oxidized and stirred in a reverberatory furnace or rotary kiln directly to form the lead monoxide.

(3) Molten lead is run into a cupelling furnace held at about 1,000 C and molten litharge is produced.

(4) Molten lead at about 500 C is atomized into a flame where it burns vigorously to yield "sublimed" or "fumed" litharge.

In all cases the product must be cooled quickly to below 300 C to avoid the formation of red lead, Pb_3O_4. In 1965, about 105,000 tons of litharge were produced in the United States. Its main uses are:

(1) in the preparation of storage battery plates (for this purpose, the partially oxidized powder, the black oxide, is more widely used than the fully oxidized product);

(2) in the ceramics industry for the manufacture of certain glasses, glazes, and vitreous enamels, and as a flux for painting of porcelain and glass;

(3) as an activator in rubber compounding;

(4) as a raw material for producing other lead compounds;

(5) in oil refining to convert the mercaptans to less evil-smelling disulfides;

(6) as a drier in varnishes;

(7) as a yellow pigment.

Lead Tetroxide[1433]

Lead tetroxide, Pb_3O_4, also known as red lead or minium, is a bright red heavy powder. In sales, it is the second most important lead oxide. In 1965, about 30,000 tons were produced in the United States. It is produced by heating the lead monoxide in a reverberatory furnace in presence of air at 450 to 500 C until the desired Pb_3O_4 content has been reached. Its major uses are:

(1) in the manufacture of storage battery plates;

(2) as a pigment in paints for protecting metal surface against corrosion and rust.

Other uses are:

(1) in glass and ceramics industries;

(2) in the manufacture of lead dioxide and matches;[1492]

(3) as a preferred raw material for making hard ferrites ($PbO \cdot 6Fe_2O_3$) which are finding rapidly expanding use as permanent magnets.

Other Lead Oxides[1433]

Lead dioxide, PbO_2, is a brown to black tetragonal crystal. It decomposes to lower oxides upon heating to 300 C or above. It is produced by anodic electrodeposition from solutions of lead salts or from lead monoxide or red lead used anodically. It is sold commercially in relatively small tonnage for use in high-voltage lightning arrestors and as an oxidizing agent in dye and chemical industries.

Lead sesquioxide, Pb_2O_3, is a black monoclinic crystal formed by hydrothermal decomposition of lead dioxide at 350 C. It has no commercial importance.

Sources and Types of Wastes

The lead oxides wastes may come from the following major sources:

(1) manufacturers of lead oxides and other lead compounds using the lead oxides as raw materials;

(2) storage battery producers and users;

(3) formulators and consumers of paints containing lead oxides;

(4) industrial plants for rubber compounding, glass and ceramics manufacturing;

(5) users of products containing lead oxides such as lead glasses, certain insecticides and ceramic products, etc.

(6) refinery storage tanks and basins.

Example of some typical waste streams containing lead oxides are:

(1) 1.5 percent lead oxide mixed with solvents, cleaners, and resins from kettle washings and equipment cleanup in paint manufacture;

(2) 1 to 2 percent lead oxide mixed with other pigments, acrylics, organic solvents, water and approximately 2.5 percent solids from paint manufacture;

(3) 15,000 ppm total lead as lead oxide and tetraethyl lead in waste oil reclaiming basins;

(4) 1 percent mixture of tegraethyl lead and lead oxide with 20 to 80 percent bottom silt and water from refinery storage tanks and basins.

Physical and Chemical Properties

The physical and chemical properties of the lead monoxide and tetroxide are given in the attached worksheets.

2. TOXICOLOGY[0766]

Lead poisoning or plumbism is one of the oldest and best known of all occupational hazards. It is caused by (1) inhalation of dusts, fumes, mists or vapors; (2) ingestion of lead compounds; and (3) absorption through the skin. However, there is no evidence that inorganic lead compounds can be absorbed through the skin in sufficient quantities to cause lead poisoning. When lead is ingested, much of it passes through the body unabsorbed, and is eliminated in the feces. The greater portion of the lead that is absorbed is caught by the liver and excreted, in part, in the bile. For this reason, larger amounts of lead are necessary to cause poisoning by the route of ingestion and a longer period of exposure is usually needed to produce the poisoning symptoms. On the other hand, when the lead is inhaled, absorption takes place easily from the respiratory tract and symptoms tend to develop more quickly. So, from the standpoint of industrial safety, inhalation of lead or lead compounds is much more important and requires more serious attention than ingestion and skin absorption of lead compounds.

Lead is a cumulative poison. Increasing amounts of lead could build up in the body. The symptoms of lead poisoning may be classified according to their clinical picture as (1) alimentary; (2) neuromotor: and (3) encephalic. The alimentary type occurs most frequently. It is characterized by abdominal discomfort or pain, constipation and/or diarrhea, nausea and vomiting, joint and muscular pains, headache and dizziness. In the neuromuscular type, the chief complaints are weakness, frequently of the extensor muscles of the wrist and hand. Joint and muscular pains are more severe. Gastroenteric symptoms are present, but not as severe. Headache, dizziness and insomnia are frequently prominent. The lead encephalopathy is the most severe but the rarest manifestation of lead poisoning. It is caused by rapid and heavy lead absorption. It begins abruptly and is characterized by signs of cerebral and meningeal involvement. There is usually stupor, progressing to coma, with or without convulsion, and often terminating in death.

For treatment of lead poisoning, it has been found that the chelating agent, calcium ethylenediaminetetracetate (Ca EDTA), and related compounds are highly efficacious in removing absorbed lead from the body tissues. Ca EDTA is effective only when administered intravenously.

The Threshold Limit Value (TLV) for lead in air recommended by the American Conference of Governmental Industrial Hygienists, 1971, is 0.15 mg/M^3.[0225] The lethal doses reported for the lead oxides are given below.[1312]

(1) lead monoxide

ip LD_{50}: 400 mg/kg, rat

(2) lead tetroxide

ip LD_{50}: 200 mg/kg, rat

The U.S. Public Health Service has established the limits and ranges of lead concentrations in public water affecting human health as follows:[1752]

(1) Physiologically safe:

Lifetime	0.05 mg/l
Short period, a few weeks	2-4 mg/l

(2) Harmful range:

Borderline	2-4 mg/l for three months
Toxic	8-10 mg/l for several weeks
Lethal	Unknown, but probably more than 15 mg/l for several weeks

Lead in soft water is highly toxic to certain fish; 0.1 mg/l is toxic to small sticklebacks; larger fish are somewhat less susceptible to lead poisoning.

3. OTHER HAZARDS

Lead tetroxide is an oxidizing agent. It would cause slight fire hazard by chemical reaction with reducing agents. Similarly, lead dioxide would react with a reducing agent. It may also ignite some organic materials when mixed. When heated to decomposition, it emits the highly toxic fume of lead.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Since lead poisoning is caused more easily by inhalation than by ingestion, adequate ventilation and dust control must be maintained to minimize the hazard of lead poisoning. Avoid breathing the lead oxide dust in handling. Wearing the dust mask approved by the U.S. Bureau of Mines for this purpose is recommended. In storage, the lead oxides should be kept away from feed or food products. As lead tetroxide is an oxidizing agent, it should also be kept away from any reducing agent to avoid fire hazards caused by chemical reactions. The lead oxides are stable chemicals under ordinary temperatures. There is no specific requirement in transportation.

Disposal/Reuse

The lead oxides (litharge and red lead) are produced in large tonnage but at a very small profit margin.[1433] Therefore, it is not economically feasible to reprocess the waste materials for reuse purpose under present circumstances. Safe disposal of lead oxide wastes is defined in terms of provisional limits as tabulated below:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Lead Monoxide	0.0015 mg/M^3 as Pb	0.01 TLV for Pb
Lead Tetroxide	0.0015 mg/M^3 as Pb	0.01 TLV for Pb

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Lead Monoxide	0.05 mg/l as Pb	U.S. Public Health Service, Drinking Water Standard for Pb
Lead Tetroxide	0.05 mg/l as Pb	U.S. Public Health Service, Drinking Water Standard for Pb

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Landfill

Since the lead oxides are insoluble in water, and also are very stable under ordinary temperatures, disposal of lead oxide wastes by means of landfill is acceptable. Mixed wastes of lead oxides such as glass and ceramic products often do not contain any water-soluble toxic components. Hence, the risk of contaminating the ground and surface waters by these waste materials is very minimal.

Option No. 2 - Conversion to Sulfide

Contaminated lead oxide wastes can be treated with nitric acid to form the nitrate which is then converted to lead sulfide by hydrogen sulfide.[0095] The sulfide precipitate can be removed by filtration and sent to lead smelter to recover its lead content.

Option No. 3 - Conversion to Carbonate

Similar to Option No. 2, the contaminated solid waste can be treated with nitric acid to yield the nitrate which is converted to lead carbonate by ammonium carbonate. The insoluble carbonate is removed by filtration and its lead content could be recovered by smelting.

In summary, the most practical method for disposal of lead oxide wastes is by landfill. However, should it be desirable or economically advantageous to recover the lead content, the waste material can be converted to lead sulfide or carbonate from which the lead content can be recovered by the smelting process. Treatment of waste streams containing both lead oxide and tetraethyl lead is discussed in the Profile Report on tetraethyl and tetramethyl lead.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Waste streams containing lead oxides and no other soluble toxic constituents or organo-lead compounds can be conveniently disposed of by landfill or by simple chemical treatment to recover the lead content. On this basis, lead oxides are not considered as candidate waste stream constituents for national disposal. However, lead oxides have also often been found in waste solvent based paint sludges, residual sludges from refinery storage tanks and basins, and sludges containing tetraethyl lead and these are candidate waste streams requiring treatment at National Disposal Sites.

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HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Lead Monoxide (242)

IUC Name

Common Names

Structural Formula

PbO

Molecular Wt. 233.19$^{(1)}$ Melting Pt. 888 C$^{(1)}$ Boiling Pt.

Density (Condensed) 9.53$^{(1)}$ @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.0017 grams/100 ml @ 20 C$^{(1)}$ Hot Water Ethanol

Others: soluble in HNO_3, alkali, lead acetate.$^{(1)}$

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead Tetroxide (242)

IUC Name ________________

Common Names ________________

Structural Formula

Pb_3O_4

Molecular Wt. 685.57(1) Melting Pt. decomposes at 500 C(1) Boiling Pt. ________

Density (Condensed) ________ @ ____ ____ Density (gas) ________ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

________ @ ________ ________ @ ________ ________ @ ________

Flash Point ________ Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower ________ Upper ________

Explosive Limits in Air (wt. %) Lower ________ Upper ________

Solubility (1)

Cold Water insoluble Hot Water insoluble Ethanol insoluble

Others: ________________

Acid, Base Properties ________________

Highly Reactive with ________________

Compatible with ________________

Shipped in ________________

ICC Classification ________________ Coast Guard Classification ________________

Comments ________________

References (1) 1570

PROFILE REPORT

Manganese (499)

1. GENERAL

Production and Use

Although the United States possesses reserves of manganese ores (greater than 35 percent Mn content) and manganiferous ores (5 to 35 percent Mn content), direct importation of ores is considered more economical than mining, so that the domestic production accounts for only 8 percent of the annual consumption (256,000 short tons ore mined vs. 3,045,000 short tons consumed in 1968).[1288] Imports account for the balance. There is virtually no recycling of used metal, although the United States Bureau of Mines has invested a great amount of experimental effort over a period of time in attempts to reclaim the 7 to 8 percent manganese contained in spent slag from basic open-hearth furnaces.[0101,0102,0103,0108,0118,0120]

Manganese is chemically and metallurgically similar to iron, and it is won from its ores by smelting in a blast furnace in a manner analogous to the smelting of iron.[1433] Occasionally low grade ores are beneficiated by leaching with sulfuric or nitric acid.[1287]

Over 90 percent of the manganese consumed is alloyed with iron and used as an additive in the production of steel.[1288,0642,1433] The most popular alloy is ferromanganese (80 percent Mn-20 percent Fe). Others include spiegeleisen (20 percent Mn-bal. Fe, C) and silicomanganese (65 to 70 percent Mn-15 to 20 percent Si). Ferromanganese and spiegeleisen are produced mostly in blast furnaces, while silicomanganese is produced in electric arc furnaces. These alloys are made and sold by many of the larger chemical companies, e.g., Foote Mineral Company, Kerr-McGee Corporation, and Union Carbide Corporation. Many steel companies, including Bethlehem Steel and U.S. Steel, produce their own.[1433]

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Approximately 1 percent of the manganese consumed (27,000 tons of ore annually) is used in the smelting of pig iron. Welding rods and fluxes account for an insignificant amount in terms of quantity, but may nevertheless pose a health hazard.[0277,0642]

The chemical industry accounts for approximately 7 percent of the total annual consumption. Most of this is refined electrolytically and converted to synthetic manganese dioxide for the production of dry cell batteries.[1288] A small amount is used as a feed additive to prevent deficiencies in livestock and as fertilizer. The Ethyl Corporation is currently in the preliminary phases of marketing manganese methylcyclopentadienyltricarbonyl as a replacement of lead tetraethyl in gasoline [0642,2128] for cars equipped with catalytic afterburners. Manganese methylcyclopentadienyltricarbonyl is discussed in the Profile Report on Manganese Methylcyclopentadienyltricarbonyl (502).

Manganese is a common impurity in coal (0.005 to 1 percent), and some is released to the atmosphere when coal is burned.[0642]

2. TOXICOLOGY

Health and Safety Standards

The Threshold Limit Value (TLV) recommended by the American Council of Governmental Industrial Hygienists is 5 mg/m^3 air.[0766] It is likely that this represents a maximum exposure limit rather than a uniformly safe standard, since disease has been reported in workers exposed to this limit. [0277,2114] The State of Pennsylvania requires a short-term maximum limit of 5 mg/m^3 for 30 min.[2112] Chronic symptoms of manganese poisoning were found at levels of 5, 6, 30, and 59 mg/m^3 air.[0277] The 1971 Annual List of Toxic Substances[1312] reports that 11 mg/m^3 by inhalation produced toxic effects in man. Both the central nervous system and the lungs were affected. Similarly, serious chronic symptoms were produced in two manganese steel workers, even though environmental assays showed manganese concentrations ranging from 2.3 to 4.7 mg/m^3 air.

Epidemiology

The only significant mode of entry is by inhalation of dusts and fumes.[2110,2111,2112,2114] The clinical symptoms have been well documented.[0277,0642,2110,2116] They primarily involve malfunctioning of the central nervous system, probably by enzyme inhibition. Warning and diagnosis is complicated by an incubation period of 6 to 30 days prior to the onset of symptoms. Definitive confirmation of manganism is by urinalysis; manganese is cumulated temporarily in the body and then discharged gradually in μg/ml quantities. $CaNa_2$ EDTA administered intravenously is effective treatment in early stages of disease. Clinical evidence shows a marked increase in urinary concentrations on administration of $CaNa_2$ EDTA, which indicates that $CaNa_2$ EDTA promotes elimination of the metal through the kidneys. A controlled, clinical study of Chilean miners suggests that a positive correlation exists between nutritional deficiency and susceptibility to manganism.

Pulmonary damage and high incidence of pneumonia have been reported among persons living in the neighborhood of manganese steel plants in Great Britain, Norway, Italy, and the U.S.S.R., but none has been reported in the United States.[0277,0642] Laboratory experiments in Great Britain and the U.S.S.R. involving intratracheal injections of manganese oxides in rats have confirmed the clinical evidence.

Inorganic and/or insoluble manganese and manganese salts administered orally are passed virtually unabsorbed. Oral administration of 100 ppm Mn stimulates animal growth, while 600 ppm proves deleterious.[0277]

3. OTHER HAZARDS

Manganese dust is a moderate hazard with respect to explosion.[0277] The minimal explosive concentration is 125 oz/1000 ft^3 and the minimum required oxygen concentration is 15 percent. At 450 C manganese dust will ignite spontaneously.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

On a worldwide basis, industrial manganese poisoning is most prevalent in the mining industry, where the mining, transporting, crushing, and sieving of the ore generate considerable quantities of dust containing manganese mixed with arsenic, lead cobalt, and nickel.[0277] No special provisions attend the shipment of the ore.

In the manufacturing of ferromanganese, steel, other metallurgical products, and in the chemical industry, waste management should involve controlling the quantity of dust emitted. Standard industrial techniques such as baghouses, electrostatic precipitators, forced ventilation, face masks, and respirators should be used to minimize worker exposure.

Disposal/Reuse

Manganese mine tailings containing less than 5 percent manganese can be discarded in the vicinity of the mine.

In steel plants, control of manganese dust is treated as part of the larger problem of general particulate emissions. Steel mill tailings contain 7 to 8 percent manganese, but as yet, despite considerable efforts, means have not been found for reclaiming the manganese economically.[0101,0102,0103,0108,0118,0120] These mill tailings contain almost all the manganese waste generated within the United States. Manganese waste as a component of steel mill tailings is discussed in the Profile Report on Mill Tailings, Lead and Zinc (276).

For the release of manganese dust particles into the environment, the acceptable criteria are defined in terms of the recommended provisional limits.

Contaminant and Environment	Provisional Limit	Basis for Recommendation
Manganese in air	0.05 mg/m^3	0.01 TLV
Manganese in water and soil	0.05 ppm (mg/l)	Drinking Water Standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Since the predominant danger with regard to manganese poisoning is by inhalation, the burial of unsegregated, nearly insoluble wastes does not constitute a significant hazard.

Disposal of Manganese Wastes

Option No. 1 - The Discarding of Manganese Dusts and Mine Tailings in the Vicinity of the Mine. These wastes are insoluble. While the situation nationally, with regard to mine tailings, is in general unsatisfactory, manganese tailings pose no special problems of their own, and comprise a small fraction of the total amount of tailings in existence.[0074] No documentary evidence was found for manganese poisoning among mine workers in the United States. This may be attributable in part to the ever-decreasing size of this industry domestically. 256,000 short tons of manganese ore were mined in the United States in 1968, compared to 302,000 tons in 1967 and 339,000 tons in 1966.[1288]

Option No. 2 - The Burial of Manganese as a Component of Steel Mill Tailings. This procedure is evaluated in the Profile Report on Mill Tailings, Lead and Zinc (276).

Option No. 3 - The Collection and Burial of Manganese Dusts at Local Plant Sites. With regard to industrial exposure, waste management practices range from satisfactory to unsatisfactory. In response to several clearly diagnosed cases of manganism from a broad segment of industry,[2112,2114] the Division of Occupation Health, Pennsylvania State Department of Health, undertook an investigation of manganese-using plants within the State of Pennsylvania.[2112] Generally, poor housekeeping and malfunctioning, poorly-maintained equipment combined to create hazardous conditions in many plants. The number of plants not complying with the Threshold Limit Value of 5 mg/m^3 listed on an industry-by-industry basis, has been presented by Tanaka and Lieben (Table 1).[2112]

TABLE 1
MANGANESE AIR EMISSIONS IN INDUSTRIAL PLANTS

Type of Industry	Total No. Plants	No. Above TLV	% in Violation
Steel	24	2	8.4
Nonferrous metals	11	0	0
Metal manufacturing	22	2	9.1
Ceramics, brick, etc.	6	1	16.7
Chemical manufacturing	5	3	70.0
Processing of ore or ferromanganese	4	4	100.0
Miscellaneous	3	0	0
Total	75	12	

In each case, compliance would not have been inherently difficult or expensive. The seriousness of the statistics is compounded by the fact that the present TLV is too high, and at best constitutes a ceiling value, rather than a true index of safety.

The situation apparently has not improved markedly in the four years since this study was made.[2129] In 1971, two new cases of manganism were diagnosed in the State of Pennsylvania. In view of the rarity of this disease and the non-specificity of its symptoms, it is probable that more were misdiagnosed. Pennsylvania may be considered typical of other states.[2129]

These dusts are insoluble, and once they are collected, their burial does not constitute a significant hazard.

With regard to the general public, extensive studies indicate that there is no air or water pollution problem at present.[0642,0768,2107,2108, 2109,2118] No documentary evidence was found for manganism among the general public. Spectrographic analyses of the water supplies of the 100 largest cities in the United States indicated a median manganese concentration of 5.0 μg/l (0.005 ppm) and a maximum manganese concentration of 1,100 μg/l (1.1 ppm). The American Water Works Assocation specifies that ideal water should contain a maximum of 0.01 ppm Mn,[2118] while the U.S. Public Health Service regards 0.05 ppm as the Drinking Water Standard.[0285] Air pollution studies indicated an average of 0.10 μg/m^3 in one study[0642] and a range of 0.005 to 1.44 μg/m^3 in another.[2106] These findings and recommendations have been summarized (Table 2). It is seen that air emissions are well below the recommended provisional limit. Water emissions are also well below the recommended provisional limit, except for several city water supplies which depend on natural ground water. These are found to be borderline acceptable.

TABLE 2

GENERAL PUBLIC EXPOSURE TO MANGANESE AIR AND WATER EMISSIONS

	Mean (or Median)	Range	Recommended
Air emissions	0.10 $\mu g/m^3$ [0642]	0.005-1.44 $\mu g/m^3$ [2106]	50 $\mu g/m^3$
Water emissions	0.005 ppm[0285]	0-1.1 ppm[0285]	0.05 ppm

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

At present, manganese does not constitute a hazard to the general public. There is evidence, however, that current industrial practices may involve exposures of workers to levels which are presently regarded as unsafe. These exposures are in the form of atmospheric dust and constitute a serious industrial health threat, since the current Threshold Limit Value itself is in need of revision downward. The problem is primarily one of dust control and ample technology is presently available to solve it with minimal economic impact.

Manganese mine tailings containing less than 5 percent Mn are not significantly different than other tailings. The suitability of taconite tailings for National Disposal Sites is discussed in the Profile Report on Taconite Tailings (419).

Similarly, the manganese contained in steel mill tailings is discussed in the Profile Report on Mill Tailings (276). Although the tailings only contain 7 to 8 percent manganese, they account for almost all the manganese waste generated in the United States.

The inadequacy of dust control within industrial plants is a problem amenable to solution by education and by application of current technology. Manganese and manganese compounds are relatively insoluble and inert unless inhaled, and while some control of their disposal as solid waste would be desirable, burial in an unsegregated manner with other wastes does not constitute a significant hazard. Manganese is therefore not a candidate waste stream constituent for national disposal.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name

IUC Name Manganese (499)

Common Names Manganese

Structural Formula

Mn

Molecular Wt. 54.9 (1)   Melting Pt. 1260 C (1)   Boiling Pt. 1900 C

Density (Condensed) 7.20 g/cc @ 20 C   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

1 mm @ 1292 C   @   @

Flash Point   Autoignition Temp. 450 C

Flammability Limits in Air (wt %)   Lower moderate (as dust)   Upper

Explosive Limits in Air (wt. %)   Lower .125 oz/1000 ft^3 (as dust)   Upper <15% O_2

Solubility

Cold Water insoluble   Hot Water insoluble   Ethanol insoluble

Others: sol. acids, insol. bases

Acid, Base Properties slightly basic

Highly Reactive with acids

Compatible with metals, oxides

Shipped in no special requirements

ICC Classification not classified   Coast Guard Classification

Comments fumes and dust hazardous if inhaled

References (1) 766

PROFILE REPORT

Manganese Sulfate (252) and Manganese Chloride (501)

1. GENERAL

Production

There are several producers of $MnSO_4$ in the United States, including the Diamond Shamrock Chemical Company, Baltimore, Maryland,[2178, 2191, 2263] Eastman Chemical Products, Inc., Kingsport, Tennessee, and the Carus Chemical Company, Inc., La Salle, Illinois.[2279] Diamond Shamrock makes $MnSO_4$ by leaching oxide ores with sulfuric acid and concentrating the filtrate. The acid insoluble residues, which consist mostly of silicon dioxide, are dried by evaporation and carted away to serve as landfill.[2178] Eastman Chemical Products and the Carus Chemical Company produce $MnSO_4$ as a byproduct of their production of hydroquinone.[2279] Aniline is oxidized by MnO_2 in the presence of H_2SO_4 to quinone. The quinone is then vacuum-distilled and reduced by iron metal filings to hydroquinone. The solid residue contains $MnSO_4$, which is isolated, crystallized, packaged, and shipped. In 1964, 34,169 tons of $MnSO_4$ were produced. Current prices range from $82 to $100/ton, depending on the manganese content.

Diamond Shamrock is the only producer of manganese chloride. The process is the same as that used for the sulfate with hydrochloric acid replacing sulfuric acid as the leaching agent. Production of $MnCl_2$ amounts to under 2,000 tons/yr, which currently sells for 21 cents/lb.

Use

Manganese sulfate is used almost exclusively for agricultural purposes.[2178, 1433] It is applied as a spray containing 4 lb $MnSO_4$/50 gal water to citrus fruits and truck crops grown in Mn-deficient soils, e.g., Florida and Rhode Island. It is an essential element in plant and animal growth. In plants it appears to catalyze the production of chlorophyll, even though it is not an integral part of the molecule, as is magnesium. Manganese sulfate is also beneficial in the neutralization of alkaline soils. Applications vary from 30 lb/acre for Rhode Island truck crops to 100 lb/acre for Florida citrus fruits.[1433] The addition of manganese sulfate to livestock feed prevents skeletal and reproductive abnormalities and disorders of the central nervous system.[0277] Typical additions are 60 mg/lb feed for poultry.[1492]

A small, undisclosed amount of manganese sulfate is used in the manufacture of pharmaceuticals.

Small quantities of manganese chloride are used in the electrolytic refining of magnesium metal.[2178, 1433] The manganese alloys with the magnesium and induces the precipitation of iron impurities. Kirk-Othmer[1433] reports that another use for manganese chloride is in the manufacture of bricks; the manganese chloride is volatilized in the kiln to impart a dark-red finish to face brick. However, communications with the Los Angeles County Air Pollution Control District [2268] and three Southern California brick manufacturers[2265, 2266, 2267] indicates that $MnCl_2$ is not used in the industry. One manufacturer does, on occasion, add manganese oxide to his charge to impart the red color. It is unlikely that brick manufacturing in other parts of the United States is conducted substantially differently, so it may be concluded that the use of $MnCl_2$ in this industry has stopped.

2. TOXICOLOGY

Manganese and manganese compounds have Threshold Limit Values (TLV) of 5 mg/M^3. Laboratory experiments with mice have shown that the approximate LD_{50} for $MnCl_2$ is 210 mg/kg administered subcutaneously and the LD_{50} for $MnSO_4$ is 44 mg/kg administered intraperitoneally.

The epidemiology of Manganese and manganese compounds is discussed more fully in the Profile Report on manganese.[0499]

3. OTHER HAZARDS

Manganese chloride and manganese sulfate are quite stable. Manganese chloride vapor reacts slowly with moist air to form HCl and MnO.[1433]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

The U.S. Department of Transportation has no special requirements or restrictions for the transportation of manganese chloride or manganese sulfate. The materials can be handled and stored with no special precautions.

Disposal/Reuse

There are no significant sources of manganese sulfate and manganese chloride wastes that could be reclaimed for their manganese values. The acceptable criteria for the release of these materials into the environment are defined in terms of the following provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Manganese chloride	0.05 mg/M^3 as Mn	0.01 TLV for Mn
Manganese sulfate	0.05 mg/M^3 as Mn	0.01 TLV for Mn

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Manganese chloride	0.05 ppm as Mn	Drinking Water Standard for Mn
Manganese sulfate	0.05 ppm as Mn	Drinking Water Standard for Mn

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Laboratory studies have shown that manganese chloride and manganese sulfate are relatively non-toxic. No incidences of poisoning in man attributable to these substances were found. These materials are quite stable and well-characterized, so it is unlikely that a future problem will arise. It may therefore be concluded that their handling, storage, and transportation are adequate.

Option No.1 - Use of Acid Insoluble Residues as Landfill

The use for landfill of the insoluble residues from the production of manganese sulfate and manganese chloride by acid leaching is satisfactory. These residues consist mostly of silicon dioxide, with some highly-insoluble manganese oxides included. There is no air emission or leaching into any ground water.

Option No. 2 - Permanent Storage in a Lagoon of Solid Waste from Hydroquinone Production

All Mn-containing waste from the production of $MnSO_4$ as a byproduct of hydroquinone is moved to a lagoon, where the manganese is precipitated with lime as $Mn(OH)_2$. The overflow from the lagoon contains less than one ppm Mn, which is below the limit set by the State of Illinois.[2279] This does, however, exceed the drinking water standard so the water should not be used as a potable source. There is no air emission except for an occasional, accidental release of quinone.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Since manganese chloride and manganese sulfate can be handled and treated adequately at the industry level, they are not candidate waste stream constituents for national disposal.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name __________

IUC Name Manganous Sulfate (252)

Common Names Manganese Sulfate

Structural Formula

$MnSO_4$

Molecular Wt. 151 (1) Melting Pt. 700 C (1) Boiling Pt. decomposes 850 C

Density (Condensed) 3.25 g/cc @ 20 C Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

______ @ ______ ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water 52 g/100 ml Hot Water 70 g/100 ml Ethanol soluble

Others: insoluble in ether

Acid, Base Properties acidic

Highly Reactive with ______

Compatible with ______

Shipped in tank cars

ICC Classification None Coast Guard Classification None

Comments no restrictions on shipment

References (1) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 501

IUC Name Manganese Dichloride

Common Names Manganese Chloride

Structural Formula

$MnCl_2$

Molecular Wt. 125.8 (1)

Melting Pt. 650 C (1)

Boiling Pt. 1190 C

Density (Condensed) 2.977 @ 25 C

Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____   ____ @ ____   ____ @ ____

Flash Point ____

Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water 62.2 g/100 ml

Hot Water 123.8 g/100 ml

Ethanol soluble

Others: insoluble in ether, NH_3

Acid, Base Properties acidic

Highly Reactive with ____

Compatible with ____

Shipped in tank cars

ICC Classification None

Coast Guard Classification None

Comments no restrictions on shipment

References (1) 1433

PROFILE REPORT

Nickel Ammonium Sulfate (290), Nickel Chloride (294), Nickel Nitrate (296), and Nickel Sulfate (298)

1. GENERAL

Introduction

Nickel ammonium sulfate [$NiSO_4 \cdot (NH_4)_2 SO_4 \cdot XH_2O$]; nickel chloride ($NiCl_2 \cdot XH_2O$); nickel nitrate [$Ni(NO_3)_2 \cdot XH_2O$]; and nickel sulfate ($NiSO_4 \cdot XH_2O$); are compounds of varying toxicity that find wide use in metal finishing, catalyst manufacture and battery manufacture, as well as minor uses in ceramics and general laboratory chemistry. Of the four compounds, nickel chloride and nickel sulfate are industrially important and their wastes are more widely spread. Nickel nitrate has limited uses while the ammonium sulfate is of little commercial significance. These four compounds represented 10 to 20 percent of the 273 million lb of nickel consumed in the United States for all purposes in 1971. The bulk of nickel is used in ferrous, non-ferrous, and high temperature alloys.[0458]

Manufacture

The production methods for nickel ammonium sulfate, nickel chloride, nickel nitrate, and nickel sulfate can be generally characterized as reactions in which the appropriate acid is reacted with a source of pure nickel metal, nickel oxide, or nickel hydroxide. The desired nickel salt products are precipitated from the mother liquor which can be reused a number of times but finally must be dumped.[2160,2162]

The purification procedures are the focal point of the technology of providing pure salts and are believed to be the major source of nickel waste from their manufacture. Due to the proprietary nature of the critical purification steps, neither the details nor their waste outputs were available.[2160] However, the major manufacturers are recovering nickel values from their waste streams before final discharge. The majority of the production is on a batch scale and soda ash (anhydrous sodium carbonate) is added to the mother liquor. The precipitated nickel carbonate is washed and is used as starting material.[2162] The contacted manufacturers also had neutralization and clarification equipment at the plant for recovering nickel and other metal ions from the unsegregated waste streams flowing from all operations at the plant. The sludges from the in-plant treatment along with insoluble filter cakes and filter aids are landfilled.[2162,2163] The levels of nickel in plant effluents after final treatment were not available because of the reluctance of plant personnel to reveal them.[2160]

Electroplating and Metal Finishing

The electroplating industry is a significant contributor, if not the major source of waterborne nickel wastes. Nickel sulfate and nickel chloride are the principal nickel salts used in the industry. Nickel ammonium sulfate has minor use to make "black nickel" surfaces. Water borne wastes in the metal finishing industry occur in six basic areas: (1) rinse water; (2) concentrated plating tanks accidentally or intentionally dumped; (3) washings from cleaning the plant equipment and facilities; (4) sludges, filter cakes, etc.; (5) regenerants or concentrates from in-plant water treating or recovery equipment; and (6) vent scrubber waters.

The predominant sources are the rinse waters, the concentrated plating baths, and sediments arising from purity maintenance on the tanks. The rinse waters are very dilute solutions containing nickel and other metals and anions, but because of their tremendous volumes, they represent the most serious pollution problem in the electroplating industry. The actual nickel plating baths can be maintained for long periods of time by means of procedures to remove impurities and maintain the effectiveness of the tank, but occasionally they are dumped and the effects of dumping such a large amount of plating solution at one time without treatment can have a disastrous effect on sewage lines, sewage treatment plants or aquatic life in open waterways. Typical effluents from metal finishing plants doing nickel plating are presented below:[0783]

TYPICAL NICKEL EFFLUENTS FROM PLATING SHOPS

Type of Work Plated	Volume gal/day	Ni Content ppm
Office machine	50,000	39
Silverware	40,000	33
Automobile manufacture	620,000	80
Metal fasteners	89,000	302

Only a very small percentage of plating shops are making any significant attempt to recover or treat waste nickel. The industry cites the lack of rigid discharge controls or limits of discharge set by municipal, state, and federal water pollution control authorities. Another reason for the prevailing discharge practices is that it is not economical to install recovery systems or plant-wide water treatment systems in the average size plating shop. Only the high waste volume platers can benefit from recovering water and metal values.[2167] Furthermore sewer authorities more or less welcome certain metal ions in their sewer lines, nickel included, which react with and precipitate free sulfides within the sewer. This removes some of the corrosive and malodorous sulfides from the domestic sewage lines. The precipitated sulfides are recovered in primary clarification steps at the sewage treatment plant and thereby do not significantly effect the operation of the plant itself. More detail on the current situation within the metal finishing industry is presented in a large number of articles, reports and books. Notably among these, are Lund's book on industrial pollution control[0285], Metal Finishing Waste Disposal (article by Ceresa and Lancy)[1119] and a state-of-the-art review of metal finishing waste treatment with an extensive bibliography prepared by Batelle Memorial Institute.[0783]

Catalyst Preparation

Nickel nitrate and nickel sulfate are used as starting materials in the preparation of nickel catalysts for the petroleum and chemical industry. The big users buy these starting materials for captive production using proprietary processes. Examples are: (1) nickel sulfate chemically reduced to a catalyst powder; and (2) nickel nitrate solution saturated on a ceramic support and gently ignited to yield the desired impregnated nickel catalyst. These processes are believed to be on a batch basis with virtually no wasting of the starting materials.[2134]

Batteries

Nickel nitrate is combined with cadmium nitrate and saturated on inert fillers for "solid" electrolyte, nickel-cadmium batteries. The consumption of nickel nitrate in batteries is minor and significant wastes from the production of these batteries or their ultimate scrapping is not believed to occur.[0356]

2. TOXICOLOGY

Generally speaking, the chloride, nitrate, sulfate and ammonium ions that are combined with nickel in the subject compounds assume the toxicological properties of the cation nickel. That is to say, if these compounds are inhaled or ingested, the toxicological effects of the nickel constituent would more likely cause a harmful effect before the ammonium, sulfate, nitrate, or chloride ions with which they are compounded.[0766]

Nickel compounds have been responsible for a variety of skin abnormalities among workers in refining plants, plating shops, and other industries where workers are in contact with them. Nickel salts have also been linked to carcinogenesis, especially when inhaled, but other materials were involved in these cases and the nickel compounds have not been proven as being singly responsible.[0615] The recommended Threshold Limit Value for airborne nickel or nickel compounds is 1 milligram per cubic meter of air.[0225] Good discussions of the health and toxicological aspects of nickel and its compounds are found in a number of published works.[0356,0615,0633]

Studies have been made to investigate the toxic effects of nickel on plant life. In general, plants are more sensitive to nickel than lead. There also is a correlation between nickel and the iron content, copper content and pH of the soil which cause significant deleterious effects.[0633]

3. OTHER HAZARDS

The sulfate and nitrate anion constituents of the compounds being discussed in this Profile Report can release toxic fumes of SO_2 or NO_2 if they are exposed to intense heat. This represents a moderate disaster hazard if large amounts of these materials are involved in a very hot fire. The nitrate ion also is a source of oxygen and if combined with combustible materials, could represent a dangerous hazard from self-sustained combustion. In general, however, these compounds are considered to be stable and present no significant hazard when stored or transported under normal conditions.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Storage, Handling and Transportation

The subject nickel salts do not require severely restrictive storage, handling and transportation procedures. All four compounds are shipped in 100-lb plastic-lined paper bags. Nickel nitrate is also commonly shipped in 400-lb steel drums. Nickel chloride and nickel sulfate are also prepared in aqueous solution convenient for electroplaters. These solutions are shipped in 5-gal pails and 50-gal steel drums. It is recommended that personnel who handle open containers of these materials be provided with protective clothing, face shields and dust filtering breathing equipment to guard against possibility of skin contact and inhalation. Solid spills should be swept up and packaged for return to the manufacturer. Liquid spills require the addition of soda ash to precipitate nickel carbonate which can be sewered with additional large amounts of water.[0095]

Disposal

The acceptable criteria for the release of nickel compounds into the environment are defined in terms of the following provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Nickel ammonium sulfate	0.01 mg/M^3 as Ni	0.01 TLV for Ni
Nickel chloride	0.01 mg/M^3 as Ni	0.01 TLV for Ni
Nickel nitrate	0.01 mg/M^3 as Ni	0.01 TLV for Ni
Nickel sulfate	0.01 mg/M^3 as Ni	0.01 TLV for Ni

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Nickel ammonium sulfate	0.05 ppm (mg/l) as Ni	Chronic toxicity drinking water studies
Nickel chloride	0.05 ppm (mg/l) as Ni	Chronic toxicity drinking water studies
Nickel nitrate	0.05 ppm (mg/l) as Ni	Chronic toxicity drinking water studies
Nickel sulfate	0.05 ppm (mg/l) as Ni	Chronic toxicity drinking water studies

Reuse

Nickel prices are currently about $1.35/lb, a level where it is apparently economical only for manufacturers and large consumers to reclaim nickel values from waste solutions.[0285,1243,2162] The smaller plating and metal finishing shops normally do not have any water recovery or solution concentrating equipment. The only conservation procedure widely used is the "save rinse" method wherein rinse water in the first, most concentrated rinsing tank is added to the electroplating tank to make up for evaporative water losses.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Introduction

The nickel compounds being considered here are almost always found as wastes in aqueous solutions and two different approaches are typically employed in the management of these solutions. The first approach of waste management is reduction of these compounds in the final plant effluent or reduction of the volume of the stream itself. This is done by: (1) changing the processes to reduce waste outputs; (2) improving housekeeping; (3) segregating waste streams with specific recovery procedures; or (4) installing equipment for recovering water and concentrating the waste stream. The concentrated waste stream can then be more easily handled. The second approach is applied to the final plant effluent to remove the contaminants with no possibilities of reusing them. This usually means removal by precipitation of sludges. Firms trying to reduce and/or recover nickel wastes employ various techniques from both approaches when dealing with their wastes. Three good sources which provide overviews of the scope of the metal finishing waste problem and the state-of-the-art on treatment methods are presented in Lund's book, an article by Ceresa and Lancy, and a report prepared by Battelle Memorial Institute.[0285,0783,1119]

Option No. 1 - Recycling and Reuse. The loss of large amounts of nickel compounds from the metal finishing industry, manufacturers and large consumers has created the need to adopt methods and equipment for recovering nickel values from these solutions. One of the easiest procedures for nickel conservation which is used in a great number of plating shops is that of "save rinse" which was described earlier. Other, more sophisticated equipment is commercially available to concentrate and recover nickel salt solutions for immediate reuse in the plant or to sell to an outside reclaiming firm. This equipment includes reverse osmosis, where the contaminated solutions are pressure-forced through a semi-permeable membrane. The permeate is recovered for rinse water and the concentrate is available for reuse or sale to a reclaimer. Multiple effect evaporators are used to concentrate solutions; thereby recovering the condensate for reuse or sale to a reclaimer as economics and purity of the concentrate dictate. The equipment also includes ion exchange which incorporates a bed of activated-beads through which the dilute aqueous solutions flow. Sites on these beads selectively attract and hold the desired ions. Periodically a regeneration solution is passed through the ion exchange beds and the adsorbed ions are desorbed from the bed in a concentrated solution. These concentrated solutions can be reprocessed for their metal values or otherwise recycled. Other newer methods are in various stages of development.

Option No. 2 - Precipitation and Clarification. Precipitation of insoluble nickel carbonate with soda ash (anhydrous sodium carbonate), or pH adjustment with caustic to yield the sludge-like, insoluble nickel hydroxide is a widely used method for treating aqueous nickel effluents. This process can produce treated effluents containing 1 to 5 ppm heavy metals when performed properly. The chemical companies manufacturing these nickel salts are actively recovering nickel from their large volume, batch, manufacturing processes for credit.[2160,2162] Whenever feasible plating shops also use soda ash to recover nickel values when a plating tank is completely rennovated. The $Ni(CO_3)_2$ can be redissolved in an appropriate mineral acid for immediate reuse, or may also be packaged, as is, for return to a reclaimer.[0285,1243,2162]

When caustic or an alkaline stream in the plant is combined with an acid plating shop effluent, the heavy metal hydroxides precipitate. These precipitates are normally gelatinous sludges with very high water content (70 to 80 percent). These sludges normally contain a wide mixture of materials and treatment after precipitation includes passage through a sand bed or similar clarifier. The sludge is removed for landfilling and the effluent is discharged to a municipal sewer or open waterway if permitted by the regulating authorities.

Option No. 3 - Direct Discharge to Municipal Sewers. Nearly all the small and medium size plating shops, and even some of the large ones, discharge their metal laden aqueous effluents to municipal sewers. Some plants have facilities to precipitate and clarify before discharge, as discussed above, but they are estimated to be about 15 percent of the total shops.[2134] In many areas, especially large metropolitan areas, this practice is allowed to continue as long as the toxicity of the nickel discharges has little or no effect on the continuous operation of any of the biological waste treatment processes of the sewage treatment plant. Many of the metal cations, nickel included, precipitate with sulfides in the domestic sewer lines while in transit to the sewage treatment plant. Thus, a great proportion of them are removed in the primary treatment process and most of the remainder are bound up in the sludge resulting from the secondary treatment processes.

The method is considered adequate provided that: (1) the sewage treatment authorities can effectively regulate the discharge of toxic metal compounds into the sewer system at a rate which will not disturb the efficiency of the sewage treatment processes; and (2) the operation and design of the sewage treatment plant is such that effective treatment is accomplished and the effluent from the treatment plant complies with the local purity regulations for discharge to open waters. The secondary sludge must be landfilled such that the provisional limits are not exceeded or they must be placed in a California Class 1 type landfill.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

National Disposal Site Facilities should not be made available to handle the subject nickel salts for the following reasons: (1) untreated wastes occur in dilute solutions that cannot be economically transported, (2) technology and waste handling techniques are available for those industries that choose to use them, and (3) wastes recovered from aqueous streams (precipitates) are being accepted by commercial dumps for landfill disposal. Landfilling these insoluble sludges or precipitates is adequate providing that the provisional limits are not exceeded or that the landfill has a proper geological location and further in either case that no materials, such as acids, are landfilled with the sludges which would cause them to redissolve and leach out. As a footnote, however, a National Disposal Site will be an excellent choice to process dried, metal laden sludges when the technology becomes available and the economics of processing are favorable. The potential for recovering metals from the tremendous volumes of these presently cumbersome and worthless materials would help in reducing the operating costs of a National Disposal Site system.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nickel Ammonium Sulfate (290)

IUC Name

Common Names double nickel salts
ammonium nickel sulfate

Structural Formula

$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Molecular Wt. 395g/mole(2)

Melting Pt.

Boiling Pt.

Density (Condensed) 1.923g/cc(1) @

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@

@

@

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 10.4g/100cc 20 C(1)

Hot Water 30g/100cc 80 C(1)

Ethanol insol

Others: Sol $(NH_4)_2SO_4$

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification

Coast Guard Classification

Comments used in electroplating

References (1) 1570
(2) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nickel Nitrate hexahydrate (296)

IUC Name

Common Names

Structural Formula

$Ni(NO_3)_2 \cdot 6H_2O$

Molecular Wt. 290.81g/mole(1) Melting Pt. 56.7 C(1) Boiling Pt. 136.7 C(1)

Density (Condensed) 2.05(1) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 238.5g/100cc @ 0 C(1) Hot Water very soluble(1) Ethanol soluble(1)

Others: NH_4OH

Acid, Base Properties aq soln:pH4

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 1570
(2) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nickel Sulfate (298)

IUC Name

Common Names

Structural Formula

$NiSO_4$*

Molecular Wt. 154.78g/mole(1)

Melting Pt. d 848 C(1)

Boiling Pt.

Density (Condensed) 3.68g/cc(1) @

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@

@

@

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 29.3g/100cc @ 0 C(1)

Hot Water 83.7g/100cc @ 100 C(1)

Ethanol Insol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification

Coast Guard Classification

Comments hexa and hepta hydrates lose water at 103 C and are more soluble in water and alcohol(1)

* Commercial products normally hydrated

References (1) 1570
(2) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nickel Chloride (294)

IUC Name

Common Names

Structural Formula

$NiCl_2$*

Molecular Wt. 129.62 C(1)   Melting Pt. 1001 C(1)   Boiling Pt. Sub 973 C

Density (Condensed) 3.55g/cc(1) @   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   1mm(2) @ 671(2) C

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water 64.2g/100cc @ 20 C(1)   Hot Water 87.6g/100cc @ 100 C(1)   Ethanol Sol

Others: NH_4OH

Acid, Base Properties aq soln is acid pH4

Highly Reactive with

Compatible with

Shipped in

ICC Classification   Coast Guard Classification

Comments Not considered a systemic poison, can cause nickel itch in plating areas(2)

* Commercial products normally hydrated

References (1) 1570

(2) 0766

PROFILE REPORTS ON THE ANTIMONY, ARSENIC, AND SELENIUM COMPOUNDS OF NICKEL

Nickel Antimonide (291), Nickel Arsenide (292), and Nickel Selenide (297)

1. GENERAL

Nickel antimonide, nickel arsenide and nickel selenide are laboratory curiosities used in gram quantities for research and development. It is believed that the major research and development activities employing the arsenide and selenide is in semiconductors.[2135] The laboratory activities using the antimonide are not known. Sources at Rocky Mountain Research indicated that they are the sole manufacturers of these materials in the United States and they knew of no imports. They estimate that the national demand for these compounds is no more than 5 to 10 lb per year for each material. The actual details of manufacture for these compounds were not available, but it is believed that the method is either to: 1) roast the nickel in antimony, arsenic or selenium vapor, or; 2) combine the elements in a sintering process.[2133] Their very small production and value would indicate, that in all likelihood, no significant amounts of the material are being lost to the environment as waste products. In addition, no evidence of any of these compounds being produced as a waste product from other unrelated processes was found.

Nickel arsenide, even though it is commercially produced in high purity, also occurs naturally as niccolite, the least of the three principal nickel ores; the others being the nickel sulfides and nickel oxides. Niccolite is said to have no current commercial importance as a nickel bearing ore.[0300] Niccolite ores are not processed in the United States and any study on NiAs wastes from foreign processing is outside the scope of this study.

2. TOXICOLOGY

The antimony, arsenic, and selenium constituents of the subject materials are the principal source behind the hazardous nature of these compounds. Most arsenic compounds are poisons whereby the systemic effects are normally caused by ingestion. As little as 0.1 grams can be fatal if taken internally. Both nickel and arsenic can be responsible for a variety of skin abnormalities on contact. Acute poisoning symptoms from ingesting arsenic compounds may include difficulty in swallowing, severe abdominal pain resulting from corrosion of the stomach lining, vomiting, with pain in the limbs and muscle cramps. A cold damp skin, a rapid and weak pulse, shock, unconsciousness and convulsions are the indicators of impending death. The symptoms caused by chronic low level arsenic exposure are difficult to diagnose due to the wide variety of unpredictable symptoms which may arise.[0766]

Selenium compounds with nickel are considered as moderate toxicological hazards that when taken orally can cause both irreversible and reversible changes that are not severe enough to cause death or permanent injury.[0766] Selenium compounds have low systemic toxicity but in dust form, they can be dangerous respiratory tract irritants as are most nickel compounds. All three compounds, when inhaled, can cause death or permanent injury even after very short exposure to small quantities.[0356] The recommended Threshold Limit Value (TLV) of 0.2 milligrams per cubic meter of air represents the maximum concentration to which personnel should be exposed in an 8-hr period. Nickel has been identified with respiratory carcinogenesis, but that is subject to debate since the cited cases involved other materials with nickel compounds.[0633]

Antimony compounds are also highly toxic when ingested or inhaled. Small amounts can cause permanent injury or death. The recommended TLV is 0.5 mg per cubic meter of air.[0766] Information on the toxicity of these compounds towards other animals and plant life was not found.

3. OTHER HAZARDS

Nickel arsenide and nickel selenide both exhibit moderate to serious fire, explosion, and disaster hazards as a result of being heated or exposed to water, steam or acids. These reactions will emit the highly flammable arsines and hydrogen selenides which, if present in the right proportions with air, could explode if ignited. Stibine (H_2Sb), arsine (H_3As), and hydrogen selenide (H_2Se) vapors are all extremely toxic and represent a serious disaster hazard if released in areas where they might be inhaled by humans or animals.[0766] Nickel antimonide and the potentially evolved hydrides of all compounds react violently with oxidizing agents.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

The toxicological and flammable hazards of these materials require careful handling when they occur as waste products in a concentrated form. They should be stored in containers in which they are compatible, i.e. screwtop glass bottles or ampules. They should be stored in cool areas with no prevalent acid mists. The use of protective clothing, eyewear and dust filtering respiratory equipment are recommended for handling these materials outside fume hoods. Spills of the solid materials should be cleaned up using a vacuum cleaner with a disposal paper dust bag. No Department of Transportation (DOT) regulations are prescribed by Sax, but common sense recommends careful labeling on both the bottle and shipping container.[0766]

Disposal/Reuse

The disposal of the antimonides, arsenides and selenides of nickel into the air, water or soil must be carefully regulated from the standpoint of the toxic nature of antimony, arsenic, selenium, and the somewhat less toxic but still significant hazard of nickel. The U.S. Public Health Service has established 0.05 mg/l arsenic content as grounds for rejecting a drinking water supply. The ideal maximum is 0.01 mg/l.[1752] The Public Health Service in its publication on drinking water standards recommended that the limits for selenium be lowered from the present value of 0.05 mg/l to 0.01 mg/l and concentrations in excess of this lower value be used as grounds for rejection of the water supply.[1752] The acceptable criteria for the release of these compounds into the environment are defined in terms of the following provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Nickel Antimonide	0.005 mg/M^3 as Sb	0.01 TLV for Sb
Nickel Arsenide	0.005 mg/M^3 as As	0.01 TLV for As
Nickel Selenide	0.002 mg/M^3 as Se	0.01 TLV for Se

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Nickel Antimonide	0.05 ppm (mg/l) as Sb	Chronic Toxicity Drinking Water Studies
Nickel Arsenide	0.01 ppm (mg/l) as As	Proposed Drinking Water Standard
Nickel Selenide	0.01 ppm (mg/l) as Se	Drinking Water Standard

All three compounds are expensive (estimated prices for ten grams each of the antimonide, arsenide, and selenide being $40, $33 and $9 respectively), and in light of this, it would appear that reasonable attempts would be made to prevent indiscriminate wasting of the compound. Small amounts of these materials, if occurring as wastes in a concentrated form, should be packaged and returned to the supplier or manufacturer for reprocessing, purification, or ultimate disposal. Considering the low levels of use for these compounds (5 lb per year), it is not expected that these materials would occur as wastes in any significant amounts. Shipping waste concentrates back to the manufacturer is the cheapest and safest way of handling them. Rocky Mountain Research, currently the only apparent manufacturer of these materials, expressed its willingness to accept returned waste concentrates.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Return to Vendor or Manufactuer

The amounts of concentrated waste nickel antimonide, arsenide, or selenide which could arise are expected to be very small. For this reason, careful packaging and shipment back to the vendor or manufacturer by prior arrangement is an easy and safe means of disposal. The manufacturer can either reprocess the material, if economically feasible, or could dispose of it in his own facilities. Return to the manufacturer or vendor should be considered before any other disposal option is considered.

Option No. 2 - Encapsulation and Landfill

Some landfills are chartered to accept these compounds for ultimate encapsulation and landfill. They would most likely be combined with other compliant materials in a steel drum, and the steel drum would be given a concrete collar before burial. Landfilling is adequate in California Class 1 type facilities.

Option No. 3 - Laboratory Decomposition to Reduce Hazard

The subject materials can be roasted in air or oxygen to produce the condensable poisonous oxides of antimony, arsenic, selenium, and non-volatile nickel oxide. The fire hazards are lower with these products, but there remains the problem of disposing the toxic products. This option offers no real advantage over Option 1 or 2.

6. APPLICABILITY OF NATIONAL DISPOSAL SITES

No recommendation is made for any equipment or waste treating processes to treat waste nickel antimonide, nickel arsenide, or nickel selenide at a National Disposal Site. It is estimated that the annual production of these materials, as wastes, does not exceed 10 pounds. Furthermore, they are rather expensive compounds and it is doubtful that they would be wasted.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nickel antimonide (291)

IUC Name

Common Names Breithauptite(1)

Structural Formula

$NiSb$(1)

Molecular Wt. 180.6(1)
Melting Pt. 1158 C(1)
Boiling Pt. d1400 C(1)

Density (Condensed) 7.54(1) @
Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@
@
@

Flash Point
Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water
Hot Water reacts
Ethanol

Others:

Acid, Base Properties

Highly Reactive with steam to form stibine(2). Can also react violently with oxidizing agents.(2)

Compatible with

Shipped in

ICC Classification
Coast Guard Classification

Comments slight explosive hazard when exposed to flame, can evolve stibine(2); releases antimony vapors when heated to decomp temp.

References (1) 1570
(2) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nickel Arsenide (292)

IUC Name

Common Names Niccolite(2)

Structural Formula

NiAs

Molecular Wt. 133.60(2)   Melting Pt. 968 C(2)   Boiling Pt.

Density (Condensed) 7.57 g/cc @ 0 C   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water insoluble   Hot Water reacts with steam   Ethanol

Others: acids (reaction)

Acid, Base Properties

Highly Reactive with hot water, steam and acids to produce toxic and flammable vapors of arsenic hydrides(2)

Compatible with

Shipped in glass bottles

ICC Classification   Coast Guard Classification

Comments Highly toxic, moderate chem. reaction to form arsine, a fire and explosion hazard.

References (1) 1570

(2) 0766

**HAZARDOUS WASTES PROPERTIES
WORKSHEET**

H. M. Name Nickel Selenide (297)

IUC Name ______

Common Names ______

Structural Formula

NiSe

Molecular Wt. 137.67(1)

Melting Pt. Red heat(1)

Boiling Pt. ______

Density (Condensed) 8.46 @ ______

Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

______ @ ______ ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water insoluble

Hot Water reacts

Ethanol ______

Others: soluble in acids; reaction

Acid, Base Properties ______

Highly Reactive with water steam and acids to produce toxic and flammable vapors of hydrogen selenide

Compatible with glass

Shipped in glass bottles

ICC Classification ______

Coast Guard Classification ______

Comments Fire hazard: evolves hydrogen selenide, a toxic gas.

References (1) 1570
(2) 0766

PROFILE REPORT

Phosphorus, White or Yellow (332)

1. GENERAL

Introduction

Elemental phosphorus has four allotropic forms, all tetra-atomic at room temperature. This Profile Report covers only the white allotrope, which is the most hazardous common form of the four, because it is highly poisonous and extremely inflammable.

White phosphorus turns yellow upon heating. It is a wax-like substance, of low melting point, very low heat of fusion, and high volatility. White phosphorus smolders and ignites spontaneously in dry air, and is usually kept under water from which all of the oxygen has been expelled by boiling. The material glows in the dark, with a yellow light.

White phosphorus is manufactured by condensing the phosphorus vapor obtained by electrothermal (electric furnace) reduction of phosphate rock with coke. The raw materials for the process are phosphate rock, coke, and silica. In 1968, over 650,000 tons of phosphorus were produced in electric furnaces in the United States[1668] by the following reaction:

$$3Ca_3(PO_4)_2 \cdot CaF_2 + 9SiO_2 + 15\ C \xrightarrow{1500C} 1\text{-}1/2\ P_4\uparrow + 9(CaO \cdot SiO_2) + 15CO\uparrow$$

The phosphorus produced is employed almost completely as an intermediate product. The largest single use is the manufacture of furnace H_3PO_4. The condensed elemental phosphorus is burned in air to produce phosphorus oxide vapor, which is reacted with water to yield phosphoric acid.

Physical and Chemical Properties

The physical and chemical properties of white phosphorus are summarized on the attached worksheet.

2. TOXICOLOGY

Elemental white or yellow phosphorus and phosphine (PH_3) are the only inorganic phosphorus compounds with recognized systemic toxicity. Skin contact with white phosphorus produces painful, slow-healing, second and third degree burns, due to both chemical and thermal damage. White phosphorus is a general protoplasmic poison when introduced via either inhalation or ingestion. Its toxicity is enhanced when the material is dissolved in solvents such as alcohol, fats or oils, or when the material is finely divided.

The acute fatal dose of white P_4 for an adult is between 50 and 100 mg, although recovery has occurred after 1.5 gm.[2376] Fatality rates are about 50 percent. Acute poisoning occurs typically in three stages. The first stage produces symptoms due to local irritation. The effects are not immediate, except for thermal burns due to contact with the body surface. Nausea, vomiting, diarrhea, and severe abdominal pain occur. If the quantity inhaled or ingested is very large, shock is severe and death may occur from cardiac collapse in the first 24 to 48 hours.[2028] The second stage is frequently symptom free, and may last from 8 hours to several weeks, with apparent recovery during this period. The third stage, involving symptoms of systemic toxicity due to the action of elemental phosphorus as a general protoplasmic poison, is normally terminated by death in 4 to 8 days, but may last as long as three weeks before death occurs. Symptoms include nausea, vomiting, diarrhea, massive hematemesis, hemorrhages into the skin, mucous membranes and viscera, liver damage including hepatic failure, cardiovascular collapse, and central nervous system involvement. If the victim survives, cerebral symptoms may continue for a protracted period.[2028]

Chronic poisoning, due to ingestion or inhalation of sub-lethal dosages produces cachexia, anemia, bronchitis, general debility and necrosis of the mandible-known as "phossy jaw".[2376]

The Threshold Limit Value (TLV) for white phosphorus is 0.1 mg per cubic meter. The provisional limits recommended for air and water are 0.001 mg per cubic meter and 0.005 mg per liter respectively.

3. OTHER HAZARDS

Phosphorus is not explosive nor is the smoke generated from its combustion. It does ignite spontaneously upon contact with air or oxygen and gives off great clouds of white smoke during combustion. Phosphorus melts at 44.1 C and when thoroughly melted, it becomes a liquid which flows and spreads even more readily than light penetrating oils or gasoline. In this form it combines readily with oxygen and burns rapidly in air. Fires can be controlled by covering with water, sand or earth to exclude air.[1881]

The P_4O_{10} fumes produced by burning phosphorus are extremely irritating, and react with any source of water to form corrosive phosphoric acid. If combustion occurs within a confined space, asphyxiation may occur due to consumption of oxygen by the burning phosphorus.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

In the manufacture of phosphorus by the electric furnace method "phossy water" containing suspended phosphorus and ferrophosphorus ore formed as waste and by-products. In handling phosphorus under water, small bits of phosphorus break off the edges of phosphorus lumps and "phossy water" is formed. The other waste stream from phosphorus production is the ferrophosphorus obtained as a by-product due to the iron content of the phosphate ores. The phosphorus content of ferrophosphorus is about 23 to 25 percent.

Phosphorus, white or yellow, is classified by the U. S. Department of Transportation (DOT) as an inflammable solid with a yellow label. It is shipped either under water or dry, by rail, water or highway. Dry phosphorus may not be shipped by rail-express, but dry shipment is rarely, if ever, used.[1881]

The Manufacturing Chemists' Association in Chemical Safety Data Sheet SD-16 summarizes the information required for white phosphorus plant design, handling, storage and shipping.[1881] Personnel handling phosphorus wastes should wear the prescribed protective clothing.

Many rat poisons and other vermin poisons contain as much as 1 to 4 percent white phosphorus, combined with such diluents as oil, flour, sugar, and coloring matter.[2028] These economic poisons remain a major source of phosphorus poisoning in humans.

Phosphorus should not be released to the environment at levels higher than those noted below. Abatement processes should convert recovered phosphorus to phosphoric acid.

The safe disposal of white or yellow phosphorus is defined in terms of the recommended provisional limits in the atmosphere and in water and soil environments. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
White or Yellow Phosphorus	0.001 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
White or Yellow Phosphorus	0.005 ppm	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The current disposal technique most frequently employed for "phossy water" is to lagoon the material in a pond within the boundaries of the electrothermal phosphorus plant. The phosphorus particles settle to the bottom of the basin, and are slowly oxidized by the oxygen dissolved in the water to hypophosphorous, phosphorous and phosphoric acids, which enter the water table. This method of disposal is not acceptable.

Ferrophosphorus is generally used as an alloying constituent in the manufacture of certain steels. The material is also subjected to destructive distillation at 1400 to 1500 C, and the phosphorus vapors produced are condensed under water.[0955, 1662] The white phosphorus thus produced is used for the same purposes as normal electric furnace phosphorus. Both of these techniques are acceptable processes for disposal via recycle and reuse.

The options listed below are those recommended for the disposal of phossy water, rat and other vermin poisons based on white phosphorus, and contaminated bulk white phosphorus.

Option No. 1 - Oxidation of Suspended Particles in Water, "Phossy Water"

Phosphorus in "phossy water" is oxidized by spraying into an incinerator equipped with an alkaline scrubber or it is oxidized by blowing through a flame followed by an alkaline scrubber.[1881]

Option No. 2 - Open Burning

Rat and vermin poisons and other solid or pasty residues containing phosphorus should be burned in an isolated location, the residue neutralized and diluted with water to a phosphate concentration less than 50 mg per liter.[0095]

Option No. 3 - Conversion to Phosphoric Acid

Contaminated phosphorus should be purified by distillation in an inert gas stream at temperatures over 280 C. The phosphorus vapor produced should be condensed under water, and recycled for sale to the furnace phosphoric acid industry. Alternatively, the contaminated phosphorus can be charged to the electric furnace used for phosphorus production.

Option No. 4 - Controlled Incineration-Municipal Incinerators

Rat and vermin poisons which contain white phosphorus and other small lots of wet phosphorus wastes, if properly segregated to permit safe handling, can be burned in municipal incinerators equipped with automatic conveying equipment and scrubbing and mist removal devices. The fly ash produced in such incinerators will generally neutralize the H_3PO_4 made.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that small quantities of white phosphorus contaminated wastes can be treated adequately by municipal incinerators as per Option No. 4 if transported sealed or under water. If large quantities of phosphorus wastes must be treated, the wastes should be shipped in air tight containers to the nearest manufacturing plant capable of recovering phosphorus via Option No. 3. It is, therefore, not recommended that provision be made at National Disposal Sites for the disposal of phosphorus.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Phosphorus, white or yellow (332)

IUC Name phosphorus, white

Common Names

Structural Formula

P_4

Molecular Wt. 124.08   Melting Pt. 44.1 C(1)   Boiling Pt. 280 C(1)

Density (Condensed) 1.82g/cc @ 20 C(1)   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point   Autoignition Temp. 30 C(1)

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water insoluble(1)   Hot Water   Ethanol insoluble(1)

Others: soluble - carbon disulfide(1)

Acid, Base Properties

Highly Reactive with oxidizing substances, air(1)

Compatible with

Shipped in sealed containers under water(1)

ICC Classification Flammable solid(1)   Coast Guard Classification Flammable solid(1)

Comments

References (1) 1416

PROFILE REPORTS ON
HALOGENATED PHOSPHORUS COMPOUNDS
PHOSPHORUS CHLORIDES

Phosphorus Oxychloride (333), Phosphorus Pentachloride (334)
Phosphorus Trichloride (336)

1. GENERAL

Introduction

Phosphorus halides were discovered and investigated by Gay Lussac and Thenard in France at the beginning of the 19th century.[1620] The best known and most studied compounds are the trihalides, pentahalides and oxyhalides. The phosphorus halides of commercial importance today are phosphorus trichloride, PCl_3; phosphorus pentachloride, PCl_5; and phosphorus oxychloride, $POCl_3$.[1433] All are used extensively in manufacturing organic phosphorus compounds and in chlorinating organic compounds to give acid chlorides.[1433,1620] Demand for the phosphorus chlorides has been steady over the past five years with phosphorus trichloride fluctuating between 50,000 to 55,000 tons per year and phosphorus oxychloride varying from 31,000 to 35,000 tons per year.[1751,2202] Production figures for phosphorus pentachloride are unavailable. The major U.S. producer is Hooker Chemical Company, Industrial Chemicals Division in Niagara Falls, New York.[2201] Future market importance and production will be affected by possible regulations on chlorinated pesticides and gasoline additives which constitute another major outlet for the phosphorus chlorides.[2202]

Manufacture

Phosphorus Trichloride: Phosphorus trichloride is manufactured by a direct union of liquid red or white phosphorus and gaseous chlorine according to the reaction:

$$2P + 3Cl_2 \longrightarrow 2PCl_3$$

Gaseous chlorine is blown into a reactor containing the liquid phosphorus and a precharge of phosphorus trichloride. The highly exothermic reaction is controlled by either refluxing cooled phosphorus trichloride or by adding carbon disulfide as an inhibitor. Crude phosphorus trichloride is then fractionally distilled to remove traces of oxychloride and organic chloride compounds.[1620,1433,2200] All reaction vessels are closed to the atmosphere and vents are equipped with refrigerated condensers to eliminate any discharge of trichloride vapors. The final vapor stream is water scrubbed to remove any final traces of trichloride.[2216] Production over the last five years was approximately 50,000 tons per year.

Phosphorus Pentachloride: Phosphorus pentachloride is manufactured either batchwise or continuously by contacting phosphorus trichloride with gaseous chlorine according to the following reaction:

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

In the batch reaction phosphorus trichloride is first dissolved in carbon tetrachloride. Chlorine is then blown over the surface of the solution causing phosphorus pentachloride crystals to form. The crystals are removed, filtered, dried (carbon tetrachloride strips off and is returned to the reaction vessel in this step) and sent to storage. The continuous reaction process produces phosphorus pentachloride by passing chlorine gas countercurrent to the phosphorus trichloride and collecting the resultant crystals at the bottom of the reaction tower.[1433,1620] Yearly United States production figures are not available in the literature and could not be ascertained during our investigation. The major producer of the pentachloride is Hooker Chemical Company in Niagara Falls, New York. Other previous manufacturers who have not continued their production are Monsanto Company and FMC Incorporated.[2202]

Phosphorus Oxychloride: Phosphorus oxychloride (also called phosphoryl chloride) is most commonly manufactured by oxidizing phosphorus trichloride with pure oxygen or air.

$$2PCl_3 + O_2 \longrightarrow 2POCl_3$$

Oxygen bubbled through liquid phosphorus trichloride at 20 to 50 C will result in a 95 to 97 percent complete reaction, so that only 3 to 5 percent trichloride remains in the oxychloride. Another well-known method of phosphorus oxychloride manufacture consists of a reaction between phosphorus pentachloride and phosphorus pentoxide:

$$P_4O_{10} + 6PCl_5 \longrightarrow 10POCl_3$$

The two solids are slowly heated and mixed until the liquid oxychloride is formed. Pure oxychloride is distilled off, cooled and sent to storage.[1433,1620] Yearly production in the United States has varied between 31,000 and 35,000 tons over the past five years with no great changes expected in the future.[1506,2202]

The bulk of the phosphorus chlorides are manufactured by four major United States corporations:[1506,2201,1411]

Monsanto Industrial Chemicals Company; Sauget, Illinois

FMC Incorporated, Organic Chemicals Division;
Nitro, West Virginia

Hooker Chemical Co.; Industrial Chemicals Division
Niagara Falls, New York

Stauffer Chemical Co.; Specialty Chemicals Division
Morrisville, Pennsylvania

Uses

All of the phosphorus chlorides are used in the manufacture of organic-phosphorus compounds. Phosphorus trichloride is used primarily as a chlorinating agent in the manufacture of organic acid chlorides. When reacted with alcohols or phenols a phosphite or phosphate ester is produced. Certain end use products are dyestuffs, organic antioxidants, vinyl stabilizers and plasticizers. Phosphorus pentachloride is similarly used as a chlorinating agent and catalyst in organic synthesis. The pentachloride is essentially a more reactive chlorinating agent than the trichloride. It recently has found additional uses as a catalyst in lubricant additive production and insecticide manufacture. Phosphorus oxychloride is one of the phosphorus-containing intermediates that may become of greater importance with an expanding plastics industry. The major portion of oxychloride produced is presently used in organic synthesis; chiefly in manufacturing phosphate esters (tricresyl phosphate, a common plasticizer). The second most important use for oxychloride is in production of cresyl diphenyl phosphate and triisopropyl phosphite, gasoline additives.[1433, 1620,2200,1411,0636,1501]

More recent uses include the organic phosphorus insecticides, parathion and methyl parathion. Other less known but increasing uses include fire resistant hydraulic fluids and flame retardants.[1433,2206]

Sources and Types of Waste

The main source of phosphorus trichloride, pentachloride and oxychloride waste is the material remaining in shipping containers after emptying. That is, the thin film left in drums and the "heel" left in tank cars and tank trucks. There are essentially no production wastes generated since all production equipment is either closed loop or equipped with refrigerated condensers to eliminate chemical emissions to the atmosphere. Storage tanks are nitrogen blanketed, pumps utilizing mechanical seals and drums are purged of air before sealing.

There are no aqueous dilute wastes. Since all three compounds rapidly decompose upon contact with water, the only source of aqueous pollution is the decomposition products, namely, hydrochloric and phosphoric acids. The concentrated wastes, however, include the unused or contaminated materials left in emptied containers and any "off-spec" production material.

Physical/Chemical Properties

Phosphrous trichloride is a fuming liquid that boils at 76 C, phosphorus pentachloride is a solid that sublimes at 148 C, while the oxychloride is a fuming liquid that boils at 107 C. Each has a specific gravity of approximately 1.6 (water = 1.0). They react violently (highly exothermic) when contacted with moisture and usually produce hydrogen chloride gas, steam, phosphoric acid and hydrochloric acid. Detailed physical and chemical properties of all three chlorinated phosphorous compounds can be found on the attached worksheets.

2. TOXICOLOGY

Phosphorus trichloride and phosphorus pentachloride are similar in toxicity in that a small amount in the atmosphere will cause prompt irritation of the eyes, nose, throat and lungs (all mucous membrane). Suffocation, bronchitis, edema and lung inflammation may all result from extended exposures. Severe exposure in a concentration of 600 ppm is lethal within a few minutes. The vapors are also irritating to the skin, while the liquid (or solid) can cause severe skin burns immediately upon contact.[1897,2205,2208] The American Conference of Governmental Industrial Hygienists 1971 recommends Threshold Limit Values (TLV) for phosphorus trichloride in air at 0.5 ppm or 3 mg/m^3; and for phosphorus pentachloride in air at 1 mg/m^3.[0225,0636]

Phosphorus oxycloride causes similar effects to the trichloride and pentachloride in that its vapors are very irritating to all mucous membranes and to the lungs. The liquid itself can cause severe burns of the skin. Inhalation symptoms range from coughing to delayed wheezing due to bronchial irritation or pulmonary edema.[2206,2207]

There is no aquatic toxicity possible from the three pure chlorinated phosphorus compounds. All readily decompose upon contact with water into hydrochloric acid and phosphoric acid. The level above which fish are affected by aqueous phosphoric acid is 0.1-10 ppm. The level above which aqueous hydrochloric acid will affect fish is 1.0 ppm.

3. OTHER HAZARDS

Phosphorus trichloride and phosphorus pentachloride by themselves are neither flammable nor explosive. However, each reacts violently with small amounts of water liberating heat, spontaneously flammable phosphine gas, hydrogen chloride, phosphorus acid and even free spontaneously flammable phosphorus. They will also react violently with slight moisture, oxidizing agents, fibrous organic matter and alkalies. The hydrochloric and phosphoric acids generated on reaction with water can attack most metals to form hydrogen gas which is both highly flammable and explosive.[1897,2205,2208]

Phosphorus oxychloride can be classified along with the other chlorinated phsophorus compounds in that it is neither flammable nor explosive. It is, however, much more corrosive in its pure state than either phosphorus trichloride or phosphorus pentachloride. Phosphorous oxychloride reacts violently with water giving off hydrogen chloride gas and steam. One gallon of water added to an excess of Phosphorus oxychloride will liberate in excess of 100 cu ft of hydrogen chloride.[1433] The reaction products, hydrochloric and phosphoric acids, can react with metals to form highly flammable hydrogen gas. Oxychloride has also displayed violent reactions with alkalies and fibrous organic matter.[2206]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

Phosphorus trichloride, phosphorus pentachloride and phosphorus oxychloride are all toxic by inhalation or skin contact. It is extremely irritating to mucous membranes and the lungs. Body moisture is sufficient to decompose them into acids which will cause severe acid burns. Full protective clothing, including gas-tight safety goggles, face shields, rubber shoes, rubber gloves and rubber apron, are required in their handling. In cases of accidental contact all contaminated clothing should be removed at once and exposed skin washed thoroughly with large quantities of water. To avoid vapor inhalation an acid-gas canister type respirator is recommended. In the event of severe exposure by inhalation, pure oxygen should be administered for at least 30 minutes.[1897,2205,2206,2207,2208]

Phosphorus trichloride and oxychloride are loaded into drums, tank cars and tank trucks at stations equipped with fume-scrubbing devices to prevent harmful vapors from reaching either the operator or the atmosphere.[2203]

Storage of small quantities of all three chemicals should be in cool, dry, well ventilated areas. Although each has a relatively high boiling point they are all very reactive with moisture in the atmosphere. Because of its corrosive nature, lead-lined, ceramic-lined or nickel-lined steel drums should be used and kept sealed from potential contact with any moisture. Large quantities are usually stored in nickel- or lead-lined steel tanks and blanketed with nitrogen. Since phosphorus pentachloride is a solid it may be stored in ordinary steel carboys or steel drums; however, the drums must be sealed tightly to avoid any contact of the pentachloride with moisture.[1897,2207]

Phosphorus trichloride and phosphorus oxychloride are classified by the U. S. Department of Transportation (DOT) as corrosive liquids. As such they must be packaged and shipped in accordance with Title 49 of the Code of Federal Regulations, Section 73.271. Phosphorus pentachloride is classified by DOT as a flammable solid and must be packaged and shipped according to Title 49 of the Code of Federal Regulations, Section 73.191.[0278]

Additional detailed information on the safe handling, storage and shipping of phosphorus trichloride and phsophorus oxychloride may be obtained by referring to Chemical Safety Data Sheets SD-27 and SD-26 published by the Manufacturing Chemists Association.

Disposal/Reuse

Contaminated lots of phosphorus trichloride, oxychloride and pentachloride are sold as contaminated or "off-spec" material. Manufacturers generally recycle and repurify any material if found to be contaminated or off-specification.[2204] The current method for disposing of small quantities of the phosphorus chlorides is to douse with copious amounts of water. Every manufacturer contacted utilizes water to dispose of small quantities of waste material.[2201,2203,2204,2216] Monsanto Industrial Chemical Division in Sauget, Illinois disposes of larger quantities (a heel from a tank car) in the following manner: They slowly add phosphoric acid to the material and then very slowly neutralize the entire mass with a sodium carbonate solution. The neutralized mass is then sewered to the waste treatment plant.[2204] The only other method feasible for disposal of large quantities is to react the phosphorus chloride slowly with copious amounts of water and neutralize the resultant acids with caustic, limestone or other basic material.

The safe disposal of these phosphorus compounds is defined in terms of the recommended provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Phosphorus oxychloride	0.07 mg/M^3 as HCl	0.01 TLV for HCl
Phosphrous trichloride	0.03 mg/M^3	0.01 TLV
Phosphrous pentachloride	0.01 mg/M^3	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Phosphorus oxychloride	0.35 ppm (mg/l)	Stokinger and Woodward Method
Phosphorus trichloride	0.15 ppm (mg/l)	Stokinger and Woodward Method
Phosphorus pentachloride	0.05 ppm (mg/l)	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Generally, phosphorus trichloride, phosphorus pentachloride and phosphorus oxychloride do not present serious pollution problems to the chemical industry because of their low volatility, easy recovery and simple decomposition as discussed below.

Removal From Air

Option No. 1 - Refrigerated Condensation. When present in sufficiently high concentrations, phosphorus trichloride and phosphorus oxychloride has been removed from vapor streams by refrigerated condensation. FMC Incorporated employs such a system in its Nitro, West Virginia production facility to control phosphorus trichloride and oxychloride emissions from its reaction equipment.[2216] The bulk of vapor is condensed and collected and trace material is removed by a final water scrubbing system.

Option No. 2 - Decomposition With Water. Most vapor streams resulting from loading operations are decomposed by a reaction of the particular phosphorus chloride compound with large volumes of water. Since phosphorus trichloride, phosphorus oxychloride,and phosphorus pentachloride rapidly decompose to hydrochloric and phosphoric acids upon contact with water,it is the cheapest most efficient method utilized. The resultant dilute acid stream is easily neutralized with caustic, soda ash, or limestone and sent to the plant sewage wastewater stream.[2201,2204,2216]

Removal From Water

All three chemicals, the trichloride, the pentachloride and the oxychloride of phosphorus readily decompose into phosphoric and hydrochloric acids upon contact with water. Consequently they do not present a water pollution hazard in their pure state. Standard neutralization techniques and dilution of the resultant stream is the simplest and cheapest technique. The danger is thereby limited to the increase of phosphate concentration leading to a possibly increased rate of eutrophication. See the Profile Report on Sodium Orthophosphates (401).

Disposal/Recovery of Concentrated Wastes

The major manufacturers of phosphorus pentachloride and phosphorus oxychloride admit that they have never had the problem of disposing of large quantities of concentrated waste material.[2201,2204,2216] The major sources of concentrated wastes are spills in loading, material left in emptied containers and "heels" left in tank cars or tank trucks.

Option No. 1 - Recycle. Waste material is easily recycled to the plant production system. Drums, tank cars and tank trucks can be drained or vacuumed to holding tanks, returned to the production process and purified. FMC Inc., Monsanto and Hooker Chemical Co. said all material returned to them is handled in this manner.[2201,2204,2216]

Option No. 2 - Decomposition. All three phosphorus compounds decompose readily in water. Therefore, flushing with water is an extremely effective and economical method of disposal. Under controlled conditions, utilizing large amounts of water, phosphorus trichloride, pentachloride and oxychloride are reacted to phosphoric and hydrochloric acids which are easily neutralized.

Option No. 3 - Chemical Degradation. Monsanto Industrial Chemicals Co. in Sauget, Illinois occasionally uses a degradation technique to scrap phosphorus trichloride and phosphorus oxychloride. The plant practice is to slowly add phosphoric acid to the material and then very slowly neutralize the mass with a sodium carbonate solution. The neutralized mass is then sewered to the waste treatment plant. This proves to be an adequate disposal technique for larger quantities of waste material.

6. APPLICABILITY TO NATIONAL DISPOSAL

It is anticipated that disposal systems to handle concentrated or dilute phosphorus trichloride, phosphorus pentachloride and phosphorus oxychloride waste material will not be required at National Disposal Sites. All waste material generated is easily decomposed, neutralized or recycled at the plant operation level.

In the event large quantities must be disposed (e.g., tank car quantity) several manufacturers said that they would recycle and reuse the "waste" material. Even without recycling, decomposition with large volumes of water would prove to be the most efficient method of disposal.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Phosphorus Oxychloride (333)

IUC Name

Common Names Phosphoryl Chloride

Structural Formula

$POCl_3$

Molecular Wt. 153.35(1)   Melting Pt. 1.22 C(1)   Boiling Pt. 107.2

Density (Condensed) 1.675 @ 20 C/4 C   Density (gas) 5.30 (air = 1.0) @ 0 C

Vapor Pressure (recommended 55 C and 20 C)

40 mm Hg @ 27.3 C   100 mm Hg @ 47.4 C   400 mm Hg @ 8.43 C

Flash Point none   Autoignition Temp. none

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility (1)

Cold Water Decomposes   Hot Water Decomposes   Ethanol Decomposes

Others: Carbon tertrachloride

Acid, Base Properties (2) Very corrosive to most common metals except nickel and lead

Highly Reactive with water, alkalies or fibrous organic matter.

Compatible with nickel and lead

Shipped in nickel lined tank cars and steel drums; 316 stainless steel tank cars(3)

ICC Classification Corrosive liquid   Coast Guard Classification Corrosive liquid

Comments A clear, colorless fuming liquid that hydrolyzed into phosphoric and hydrochloric acids. It volitizes quickly upon contact with water giving off hydrogen chloride gas. Acids formed can react with metals to give off highly flammable hydrogen gas.

References (1) 2206, 1570
(2) 2207
(3) 2216

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Phosphorus Pentachloride (334)

IUC Name

Common Names same

Structural Formula

PCl_5

Molecular Wt. 208.3(1)

Melting Pt. 148 C under pressure(1)

Sublimes at 160 C(1)

Density (Condensed) 1.6 @ 20 C/4 C

Density (gas) 4.65 g/l @ 296 C

Vapor Pressure (recommended 55 C and 20 C)

1 mm Hg @ 55.5 C(2)

10 mm Hg @ 83.2 C

100 mm Hg @ 117 C

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Decomposes

Hot Water

Ethanol

Others: Carbon tetrachloride, Carbon disulfide, Benzoyl chloride

Acid, Base Properties not corrosive per se--upon reaction with water hydrochloric and phosphoric acids are created.

Highly Reactive with water (moisture) to form toxic and corrosive fumes--potentially explosive if phosphine is formed.

Compatible with non-corrosive materials (e.g., nickel, 316 stainless steel, lead).

Shipped in plastic lined steel drums or carboys.

ICC Classification flammable solid

Coast Guard Classification inflammable solid

Comments Decomposes upon contact with water or heat into hydrogen chloride, phosphorus oxides, phosphorus oxychlorides; flammable phosphine possible. Pentachloride is a yellow white crystalline substance extremely more reactive than phosphorus trichloride.(3)

References (1) 1570, 2208
(2) 1673
(3) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Phosphorus Trichloride (336)

IUC Name

Common Names Phosphorus Chloride

Structural Formula

PCl_3

Molecular Wt. 137.35(1)   Melting Pt. -118.5 C(1)   Boiling Pt. 75.5 C(1)

Density (Condensed) 1.575 @ 20/4 C(1) (ref = water)   Density (gas) 4.75 @ 0 C(1) (air = 1.0)

Vapor Pressure (recommended 55 C and 20 C)

400 mm Hg @ 56.9 C-(1)   100 mm Hg @ 21 C-(1)   @

Flash Point Nonflammable-(2)   Autoignition Temp. none

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility (1)

Cold Water Decomposes   Hot Water Decomposes   Ethanol Soluble

Others: Chloroform, Ether, Benzene, Carbon Disulfide, Carbon Tetrachloride

Acid, Base Properties Corrosive to most metals except nickel and lead(2)

Highly Reactive with water and aqueous solutions, oxidizing agents, fibrous organic matter, alkalies.

Compatible with nickel, lead, 316 stainless steel

Shipped in Carbon steel tank cars, lead or nickel lined steel drums

ICC Classification Corrosive liquid   Coast Guard Classification Corrosive liquid

Comments Colorless fuming liquid with pungent, irritating odor resembling that of hydrochloric acid. Contact with water decomposes PCl_3 into hydrochloric and phospheric acid.(3)

References (1) 2205, 1570
(2) 1897
(3) 2216

PROFILE REPORT

Phosphorus Pentasulfide (335)

1. GENERAL

Phosphorus pentasulfide is one of only four phosphorus-sulfur compositions which are definite chemical entities. It is the largest volume phosphorus sulfide produced. Phosphorus pentasulfide (chemical name, tetraphosphorus decasulfide) is referenced in the literature as P_2S_5, however, the yellow-green crystals manufactured in bulk quantity exist in the P_4S_{10} state.[1620,1433,2209]

Modern commercial preparation of phosphorus pentasulfide is carried out by reacting white phosphorus and elemental sulfur continuously at about 350 C. It is also made in commercial quantities by heating elemental sulfur with red phosphorus in a batch process. When the molten phosphorus pentasulfide is cooled properly it consists almost completely of crystalline P_4S_{10}.[1620] The crystals are then purified by washing with carbon disulfide to remove small percentages of phosphorus sesquisulfide and free sulfur. In 1971 approximately 70,000 tons of phosphorus pentasulfide was produced by these three major manufacturers:

Monsanto Company: Industrial Chemicals Unit,
Sauget, Illinois

Hooker Chemical Co.: Industrial Chemicals Division
Niagara Falls, New York

Stouffer Chemical Co.: Specialty Chemicals Division
Morrisville, Pennsylvania

This represents almost a 100 percent increase in production since 1965 when U.S. production was marked at 34,000 tons.

The major impetus behind the growth of phosphorus pentasulfide has been its continued demand in the expanding manufacture of organic phosphorus compounds used as plasticizers and in insecticide production. A more recent and expanding use is in the production of thio-phosphate esters used in gasoline and oil additives.[1433,1620,2200] The largest single-volume items produced are the dithiophosphates used in the manufacture of parathion and methyl parathion and oil additive zinc dithiophosphate. Extensive government pollution control legislation could materially affect the use of parathion, methyl parathion and zinc dithiophosphate which, in turn, would reduce the production of phosphorus pentasulfide significantly.

Sources and Types of Wastes

The main sources of phosphorus pentasulfide waste may include: (1) the manufacturer of the chemicals; (2) pesticide formulators; (3) oil additive producers; (4) storage facilities and (5) shipping containers.

In general, the only wastes possible are the concentrated crystalline pentasulfide material. Consequently, unused or contaminated materials left in shipping containers or spillage constitute the major sources of concentrated waste.

There are essentially no diluted wastes associated with phosphorus pentasulfide due to its rapid decomposition upon contact with water. The following equation typifies the reaction of phosphorus pentasulfide with water:

$$P_4S_{10} + 16H_2O \longrightarrow 4H_3PO_4 + 10H_2S$$

Physical and Chemical Properties

Phosphorus pentasulfide is a gray to yellow-green solid with a specific gravity of 2.03 (water = 1.0), a melting point of 296 C and a boiling point of 513 C. It exists as a dry non-corrosive powder which is flammable.[1620,2209,2217] Detailed physical and chemical properties are contained in the attached worksheet.

2. TOXICOLOGY

Phosphorus pentasulfide is only a mild irritant in its pure solid state. It can cause slight skin irritation upon contact and serious irritation to the eyes and mucous membranes. Effects of inhalation or ingestion range from minor irritation and coughing, to respiratory failure.[0766,2217] The American Conference of Governmental Industrial Hygenists recommends a Threshold Limit Value (TLV) of 1.0 mg/m^3 of air.

The major hazard associated with phosphorus pentasulfide is a result of the rapid decomposition of P_4S_{10} upon contact with moisture into toxic and flammable hydrogen sulfide and phosphoric acid.

$$P_4S_{10} + 16H_2O \rightarrow 4H_3PO_4 + H_2S$$

The ACGIH recommended TLV for H_2S is 10 ppm or 15 mg/m^3. At high concentrations it has a paralyzing effect of the olfactory nerves and therefore cannot be detected by odor. Phosphorus pentasulfide is also extremely dangerous when heated. The fumes emitted are phosphorus pentoxide which has a recommended TLV of 0.1 mg/m^3 of air, and oxides of sulfur which are also toxic (TLV of 5 ppm for SO_2).

Water pollution hazards associated witn pure phosphorus pentasulfide are negligible because of its rapid decomposition.[0766,2209,2217]

3. OTHER HAZARDS

Phosphorus pentasulfide is ignitable by friction, by static, and by struck sparks at room temperature. It will spontaneously ignite at temperature near its melting point of 280 C. At low temperatures it burns slowly unless it is dispersed in air where it burns rapidly. The dust of pentasulfide presents an explosion problem. In addition, flammable hydrogen sulfide gas is liberated in the presence of moisture. Phosphorus pentasulfide has also been known to react with acids and oxidizing agents to yield the same products as the reaction with water.[2209]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

Phosphorus pentasulfide must be handled with care to avoid the generation of hydrogen sulfide vapors, the hazards of dust explosion and hazards of spontaneous ignition. However, since phosphorus pentasulfide is not corrosive it does not require any special materials of construction in its production. It must, however, be stored in a cool, dry, non-combustible ventilated area separated from other combustibles, acids or oxidizing materials. Equipment must be grounded to avoid friction sparks. Inert nitrogen is recommended as the best protection against explosion, toxicity and hydrolysis dangers.[2217] Personnel should have chemical safety goggles, rubber gloves and rubber shoes to prevent contact with the skin. Also self-contained breathing apparatus or externally supplied air masks should be located nearby in the event of H_2S emission.

Phosphorus pentasulfide is not classified as a dangerous article by the Department of Transportation for the purpose of transportation. The usual shipping containers are fiber or steel drums and aluminum tote bins. Most manufacturers and users who utilize tote bins design their equipment so that the tote bin is filled, sealed, shipped and emptied without ever being open to the atmosphere. This eliminates most of the hazards associated with the chemical.[2201]

Disposal/Reuse

Contaminated or degraded phosphorus pentasulfide is usually not considered for reprocessing, although manufacturers would normally accept it for disposal. As mentioned in the previous section, manufacturers and users minimize their waste material by using equipment which minimizes contact with the atmosphere.

The safe disposal of phosphorus pentasulfide is defined in terms of the recommended provisional limits:

Contaminant and Environment	Provisional Limit	Basis for Recommendation
Phosphorus pentasulfide in air	0.01 mg/M^3	0.01 TLV
Phosphorus pentasulfide in water and soil	0.05 ppm (mg/l)	Stokinger and Woodward Method

Careful consideration must also be given to the decomposition product hydrogen sulfide which has a recommended provisional limit of 0.15 mg/M^3 in air.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Since phosphorus pentasulfide is a powdered solid with a very low vapor pressure it does not present an air pollution problem. The only source of waste is the solid scrap material accumulated from spills in manufacturing or loading.

Option No. 1 - Decomposition with Water

Several manufacturers of phosphorus pentasulfide recommend dousing small quantities of the chemical with copious amounts of water, while taking precautions to keep hydrogen sulfide generation at a low level.[2201,2204] Large volumes of water keep the decomposition temperature low,thereby reducing the H_2S emission rate. The aqueous decomposition product (phosphoric acid) can then be treated by standard industrial wastewater treatment techniques (e.g., neutralization).[2201,2217]

Option No 2. - Burial

Phosphorus pentasulfide can be buried in a sanitary landfill disposal site. This essentially is a slow hydrolysis process which must be carefully done to minimize the evolution of hazardous hydrogen sulfide. Very small quantities may be adequately handled in this manner.[2204,2209]

Option No. 3 - Incineration

Phosphorus pentasulfide can be incinerated to yield phosphorus pentoxide (P_2O_5) and sulfur dioxide (SO_2). Large quantities of waste material should be disposed of by incineration only where the combustion equipment is capable of removing the combustion products from the exhaust gas stream.[2217,2209]

Option No. 4 - Neutralization

Phosphorus pentasulfide rapidly decomposes upon contact with water into phosphoric acid and gaseous hydrogen sulfide. Therefore, it does not present a water pollution hazard in its pure chemical state. Standard neutralization techniques and dilution of the resultant stream are the simplest and cheapest method of disposal. The danger is thereby limited to the increase in phosphate concentration which could possibly lead to an increased rate of water eutrophication.

6. APPLICABILITY TO NATIONAL DISPOSAL SITE

It is anticipated that disposal systems to handle waste streams containing phosphorus pentasulfide will not be required at National Disposal Sites. All waste material generated is easily decomposed, neutralized or recycled at the plant operation level.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Phosphorus Pentasulfide (335)

IUC Name Tetrophosphorus Decasulfide

Common Names Thiophosphoric Anhydride

Structural Formula

P_4S_{10}

Molecular Wt. 444.56 (1) Melting Pt. 286 C (1) Boiling Pt. 513 C (2)

Density (Condensed) 2.03 @ 20 C (1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

1 mm Hg @ 300 C @ @

Flash Point Autoignition Temp. 260 290 C (dust)
275 C (liquid)

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower 0.050 oz/cuft Upper
(200 mesh dust in air)

Solubility

Cold Water Decomposes (2) Hot Water Ethanol

Others:

Acid, Base Properties dry powder noncorrosive

Highly Reactive with water to form toxic, corrosive, flammable hydrogen sulfide. Reactive with acids and oxidizing agents also.

Compatible with mild steel.

Shipped in fiber and steel drums or aluminum tote bins.

ICC Classification Coast Guard Classification

Comments A yellow green powder which will: (1) react with water to form hydrogen sulfide; (2) ignite by spark or friction; (3) explode when dispersed as a dust; (4) decomposes into toxic and corrosive sulfur dioxide and phosphorus pentoxide.

References (1) 2209, 2217
(2) 1620

PROFILE REPORT

Potassium Permanganate (349)

1. GENERAL

Potassium permanganate forms glittering dark purple crystals with a sweetish astringent taste. It is a strong oxidizing agent that decomposes at 240 C with the liberation of oxygen.

Potassium permanganate is prepared in two stages. In the first stage manganese dioxide (tetravalent Mn), is oxidized to manganate (hexavalent Mn) by passing an ore containing manganese dioxide mixed with a 50 percent solution of potassium hydroxide and steam through a series of rotary kilns. In the second stage of the process, the potassium manganate is dissolved in water, filtered and oxidized to potassium permanganate, either in an electrolytic cell or in a chemical process, In the chemical oxidation process, the filtered solution of potassium manganate is neutralized with carbon dioxide and heated; two-thirds of the potassium manganate is oxidized to potassium permanganate and one-third is reduced to manganese dioxide.[1433]

The uses of potassium permanganate depend on its oxidizing power. Important quantities are used for production of saccharin and benzoic acid since potassium permanganate oxidizes the methyl group of toluene and toluene derivatives to a carboxylic acid group. Manganese dioxide is obtained as a by-product. Potassium permanganate is also used for bleaching and decolorizing such materials as oils, fats, waxes and natural sponge. It is also used in textile bleaching, as a disinfectant and antiseptic for staining wood, and for forming tightly adherent oxide coatings on aluminum.[1433] Recently it has found considerable use in treating wastes such as phenols, aldehydes, ketones, esters, olefins, mercaptans, amines, tannins, lignins, hydrogen sulfide and lower oxides of nitrogen.[2300]

The physical/chemical properties of potassium permanganate are summarized on the attached worksheet.

2. TOXICOLOGY

Potassium permanganate solutions and dust are strong irritants to the eyes, nose and throat, and ingestion must be avoided during ordinary handling and storage operations. Prolonged ingestion of manganese compounds can produce chronic manganese poisoning, but the irritant effects from potassium permanganate would be so pronouced as to require treatment prior to the onset of any chronic toxic effects.[0766]

Drinking water standards limits $KMnO_4$ concentration to 0.05 mg/l. The critical $KMnO_4$ concentration for fish toxicity is 3 mg/l.

3. OTHER HAZARDS

Potassium permanganate is a powerful oxidizing agent that is spontaneously flammable on contact with glycerin, ethylene glycol, and numerous other organic materials. It may detonate when severely shocked or exposed to high temperature.[2300] Storage of potassium permanganate in a cool, dry, fireproof building is recommended. Dry concrete floors are preferred to wooden floors. The material should be stored away from acids, organic solvents, oils and combustible materials.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Direct contact of potassium permanganate with reducing agents and organic materials should be avoided. Dry potassium permanganate is not corrosive to most metals. It may etch glass because it contains traces of potassium hydroxide. In neutral solutions, it is not corrosive to iron, aluminum, lead, zinc and alloys containing these metals. It attacks rubber and most fibers.

Potassium permanganate is shipped under Department of Transportation (DOT) regulations for an oxidizing material. Small quantities are packaged in bottles or jars, with larger quantities shipped in steel drums containing 85 to 600 lb. The bulk material may also be shipped in hopper cars and trucks.[2300]

Disposal/Reuse

Potassium permanganate is an oxidizing agent commonly employed in waste water treatment and its presence up to a certain concentration in waste streams could be considered as beneficial. Because manganese dioxide, the reduction product of potassium permanganate, is insoluble, the manganese in potassium permanganate waste streams may be a mixture of soluble potassium permanganate and manganese dioxide sludge. The acceptable criteria for the release of potassium permanganate into the environment is defined in terms of the following provisional limits:

Contaminant and Environment	Provisional Limit	Basis for Recommendation
Potassium permanganate in air	0.05 mg/M^3 as Mn	0.01 TLV for Mn
Potassium permanganate in water and soil	0.05 ppm (mg/l) as Mn	Drinking water standard for Mn

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Potassium permanganate is a valuable material that is often used to treat waste streams containing oxidizable substances. It is not anticipated that large quantities of potassium permanganate will ever require treatment as a waste. When disposal of waste or contaminated potassium permanganate is required, reducing substances such as phenolic wastes, sugar solutions or formaldehyde wastes can be added to a dilute solution of the potassium permanganate waste, maintaining a pH of 9 to 10. The potassium permanganate is reduced to the insoluble, colloidal hydrous manganese dioxide which should be removed by flocculation and lagooning, and placed in an appropriate landfill.[2300]

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Since most potassium permanganate wastes are likely to be discharged as relatively dilute solutions, the material is not considered economically feasible for National Disposal Site processing, and is not recommended as a candidate waste stream constituent for National Disposal Sites. The simple method outlined in Section 5 for the reduction of potassium permanganate to insoluble manganese dioxide can be performed by any firm that handles potassium permanganate wastes.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Potassium Permanganate (349)

IUC Name Potassium Permanganate

Common Names

Structural Formula

$KMnO_4$

Molecular Wt. 158.03(1) Melting Pt. 240 C decomposes(1) Boiling Pt.

Density (Condensed) 2.7 g/cc @ 23 C(1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 6.3 g/100 g at 20 C(1) Hot Water Ethanol reacts(1)

Others: reacts with most organic solvents(1)

Acid, Base Properties

Highly Reactive with reducing substances(1)

Compatible with

Shipped in Hopper cars or steel drums(1)

ICC Classification oxidizing material, yellow label(1) Coast Guard Classification oxidizing material, yellow label(1)

Comments

References (1) 1433

PROFILE REPORT

Potassium Peroxide (350), Sodium Peroxide (400), Sodium Monoxide (508)

1. GENERAL

There is apparently only one domestic manufacturer of sodium peroxide, Reactive Metals,[1296] Ashtabula, Ohio, a subsidiary of U.S. Industrial Chemicals, which in turn is a subsidiary of the National Distillers and Chemical Corporation. The peroxide is produced by controlled oxidation of sodium metal with no waste. The primary use is for bleaching in the pulp and paper industry. No production figures are available, but the market is decreasing as paper manufacturers are switching to hydrogen peroxide and sodium hypochlorite, and it is anticipated that the demand will approach zero within several years.[1296] Except for the odd 5-lb can, none has been sold in California for several years.[1295] Three major pulp and paper producers were contacted, Crown Zellerbach,[1289] Weyerhauser,[1290] and Georgia-Pacific.[1291] Their environmental staffs and purchasing agents know of no sodium peroxide use at present.

Neither Sitting[0274] nor Kirk-Othmer[1433] report any commercial use for sodium monoxide. It can be prepared by the controlled burning of sodium in air at temperatures less than 160 C. It appears in the waste sludge in the production of sodium metal in an intimate mixture with Na, Ca, and CaO[1433, 0595] and in used sodium as the principal contaminating material. In this latter form, it promotes corrosion and fouls pumping equipment. With sodium now selling at 23¢/lb, Atomics International,[0398,0399] a large sodium user, finds it more economical to dispose of the sodium metal than to repurify it. Thus, sodium monoxide waste disposal is part of the sodium metal disposal problem, which is discussed in the Profile Report on sodium metal (374).

There are two commercial uses for potassium in the United States--as a component of NaK for catalysis and cooling systems and for the production of K_2O_2 for use in breathing apparatus. Total potassium production is 100 tons/yr by a sole supplier, MSA,[0395] and is expected to remain constant over the next 10 years. The quantity breakdown of this production into NaK and K_2O_2 is unavailable. Kirk-Othmer[1433] reports the production process to be:

$$\mathrm{Na} + \mathrm{KCl} \longrightarrow \mathrm{NaK} + (\mathrm{Na, K})\,\mathrm{Cl} \xrightarrow{\text{distillation}} \mathrm{K} \xrightarrow{\text{dry } O_2} \mathrm{KO_2} \xrightarrow{\text{decomposition}} \mathrm{K_2O_2}$$

There is no appreciable K_2O_2 waste either at the source or from any individual spent breathing apparatus.

The waste products from the NaK and K production are the oxides and chlorides of sodium and potassium. MSA would not release any waste production figures, but did say that the oxides are neutralized in settling ponds and then discharged into nearby rivers. The mixed chlorides are trucked to a nearby abandoned mine.

2. TOXICOLOGY

These materials are dangerous due to their caustic properties. The 1971 Annual List of the U.S. Department of Health, Education, and Welfare does not list these as toxic substances.[1312] Sax[0766] does not report a Threshold Limit Value (TLV) for these materials, but NaOH, which forms vigorously on contact of Na_2O or Na_2O_2 with moisture or human tissue, has a TLV of 2 mg/m^3, as recommended by the American Conference of Governmental Industrial Hygienists. The hydroxides themselves are caustic in concentrated form, but neutralization with acid renders them harmless.

3. OTHER HAZARDS

The oxides and peroxides of sodium and potassium react vigorously with water, acids, and powdered metals.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

Sodium peroxide and potassium peroxide are strong oxidizing agents and sodium monoxide is a strong drying agent and caustic. Extreme caution should be exercised in their handling. Protective clothing, rubber gloves, a full face shield, and a dust respirator should be worn. In case of heavy dust concentration in air, the use of chemical safety goggles is recommended. Contaminated clothing, including shoes, should be immediately removed and thoroughly cleaned before reuse. In cases of fire, only dry chemicals should be used as extinguishing agents.

All three oxides should be stored in cool, dry, well-ventilated, and preferably fire-resistant areas. The containers for these chemicals should also be kept off from the floor, and away from any possible contacts with water, combustibles, and organic or readily oxidized substances.

Sodium peroxide and potassium peroxide are classified by the U.S. Department of Transportation (DOT) as Oxidizing Material. As such, both chemicals must be packed in DOT specification containers when shipped by rail, water, or highway and all DOT regulations governing loading, handling, shipping and labeling must be complied with. Sodium monoxide is not classified by DOT, but as a strong caustic, the regulations governing the handling, loading, and shipping of sodium hydroxide should be followed.

Disposal/Reuse

Sodium monoxide, sodium peroxide, and potassium peroxide all react violently with water to form either sodium or potassium hydroxides. No

Threshold Limit Value (TLV) for these chemicals have been reported. For the safe disposal of these materials, the recommended provisional limits are as follows:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Sodium monoxide	0.02 mg/M^3 as NaOH	Provisional limit for NaOH
Sodium peroxide	0.014 mg/M^3 as H_2O_2	0.01 TLV for H_2O_2
Potassium peroxide	0.014 mg/M^3 as H_2O_2	0.01 TLV for H_2O_2

Contaminant in Water and Soil	Provisional Limits	Basis for Recommendation
Sodium monoxide	0.1 ppm as NaOH	Provisional limit for NaOH
Sodium peroxide	0.1 ppm as NaOH	Provisional limit for NaOH
Potassium peroxide	0.1 ppm as KOH	Provisional limit for KOH

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The oxide waste from the production of NaK by MSA[0395] is neutralized with sulfuric acid in settling ponds and discharged into nearby rivers.

The small concentration of several percent Na_2O which appears as a contaminant of Na metal is treated with the metal in an unsegregated manner. As a component of breathing apparatus, K_2O_2 is converted to KOH and O_2. The KOH produced is likely present in too small amounts to be considered a significant hazard.

Any Na_2O_2 used for bleaching in the pulp and paper industry would be reduced in the effluent streams to NaOH.[1289,1290,1291] If the total stream is caustic it should be neutralized with acid prior to sewering.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Sodium peroxide and potassium peroxide are not found in any appreciable amounts as waste stream constituents. The only significant source of sodium monoxide waste is in the waste sludges of sodium metal production, and these are currently disposed of by dumping at sea in perforated drums so that complete reaction to sodium hydroxide is attained. Since all three compounds are adequately handled at the industrial level, they are not considered as candidate waste stream constituents for national disposal.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ______________

IUC Name SODIUM MONOXIDE (508)

Common Names SODIUM OXIDE

Structural Formula

Na_2O

Molecular Wt. 61.99 Melting Pt. 920 C Boiling Pt. 1350 C(decom

Density (Condensed) 2.27 g/cc@ ______ Density (gas) ______ @ ______

Vapor Pressure (recommended 55 C and 20 C)

______ @ ______ ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower not flam. Upper not flam.

Explosive Limits in Air (wt. %) Lower not flam. Upper not flam.

Solubility

Cold Water decomposes Hot Water decomposes Ethanol decomposes

Others: ______

Acid, Base Properties strongly basic

Highly Reactive with water, powdered metals, steam, acids

Compatible with oxides

Shipped in ______

ICC Classification none Coast Guard Classification hazardous material

Comments obtained when Na burned <160 C

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ____________

IUC Name SODIUM PEROXIDE (400)

Common Names SODIUM DIOXIDE, SODIUM SUPEROXIDE,

Structural Formula

Na_2O_2

Molecular Wt. 77.99 Melting Pt. 460 C Boiling Pt. decomposes 651

Density (Condensed) 2.805 g/cc @ ____ ____ Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____ ____ @ ____ ____ @ ____

Flash Point ____ Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower Dangerous Upper ____

Explosive Limits in Air (wt. %) Lower Moderate Upper ____

Solubility

Cold Water decomposes Hot Water decomposes Ethanol decomposes

Others: dil. acid, decomposes in NH_3 (aq.)

Acid, Base Properties strongly basic

Highly Reactive with water, powdered metals, steam, acids evolving heat, combustible material

Compatible with oxides

Shipped in ~~75 lb steel pails and 400 lb steel drums @ 20¢/lb~~

ICC Classification oxidizing material, yellow label, 100 lb Coast Guard Classification oxidizing material, yellow label

Comments Sec. 78.187
obtained when Na burned >160 C

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name ______________

IUC Name POTASSIUM PEROXIDE (350)

Common Names POTASSIUM PEROXIDE

Structural Formula

K_2O_2

Molecular Wt. 110.19 Melting Pt. 490 C Boiling Pt. ________

Density (Condensed) ________ @ ____ ____ Density (gas) ________ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

________ @ ________ ________ @ ________ ________ @ ________

Flash Point ________ Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower Dangerous Upper ________

Explosive Limits in Air (wt. %) Lower Moderate Upper ________

Solubility

Cold Water Decomposes Hot Water Decomposes Ethanol Decomposes

Others: ________

Acid, Base Properties Strongly basic

Highly Reactive with Spontaneously, water, steam, acids, powdered metals

Compatible with oxides

Shipped in steel pails

ICC Classification Oxidizing material, yellow la , 100 lb Coast Guard Classification oxidizing material, yellow label

Comments Sec. 73.154

Obtained either by oxidizing K in liq. NH_3 sol. or decomposing KO_2-disproportionat

easily

PROFILE REPORT

Selenium (367)

1. GENERAL

Production

There are five selenium producers in the United States[1288]: American Metal Climax, Carteret, New Jersey; American Smelting and Refining Company, Baltimore, Maryland; International Smelting and Refining Company, Perth Amboy, New Jersey; Kennecott Copper Company, Garfield, Utah; and KBI Industries, Boyertown, Pennsylvania. KBI processes materials produced by the mining operations of the other four, supplemented by imports. Almost all production is as the by-product of the electrolytic refining of copper, gold, nickel, and silver ores, with copper ore accounting for over 90 percent of the 600,000 lb produced annually in the United States. An additional 400,000 lb is imported to make up the 1,000,000 lb annual domestic consumption. A small amount is also produced as a by-product of lead refining and sulfuric acid production. The weakness of the market precludes the exploitation of selenium ores directly and this situation is likely to continue indefinitely.[1287] In fact, demand is so slack relative to the copper market, that only 60 percent of the potentially winnable selenium is recovered as the by-product.

At $4.50/lb of the commercial grade (99 % pure) and $6.00/lb for the high purity grade (99.99 % pure), [1288] selenium is considered of sufficient value for secondary recovery. Approximately 30,000 lb are recovered each year from spent catalysts, factory scrap, and xerographic cylinders, and sold back to the primary producers for recycling.

Typically, selenium is won from the anode mud or slime resulting from the electrowinning of copper. There are two basic methods: (1) smelting or roasting the mud with soda ash to form the water soluble Na_2SeO_3, followed by neutralization with acid to precipitate tellurium metal, and filtration and acidification with SO_2 gas to precipitate selenium metal or (2) heating the mud with H_2SO_4 to volatilize the selenium as SeO_2, followed by collection as H_2SeO_3 in a wet Cottrell precipitator, and further acidification with SO_2 gas to precipitate selenium metal. Approximately 250 people are employed in selenium production, purification, and fabrication in the United States.

Uses[1433,1748,1287,1288,0277]

Two unique properties make selenium virtually irreplaceable for a wide variety of applications. It is an excellent decolorizer for glass and it is a semiconductor whose electrical conductivity varies strongly as a function of the incident light. This light sensitivity makes selenium and its compounds ideal for "electric-eye" systems and for xerography, where a selenium-containing powder is charged and exposed selectively to light to discharge the exposed areas. The undischarged areas are then fixed. Selenium rectifiers are popular because selenium can be easily made to conduct current in the forward, but not in the reverse direction.

The glass industry accounts for about 31 percent of the annual selenium consumption, duplicating machines account for another 22 percent, electronics and power transmission account for 16 percent, and the paint and pigments industry (as cadmium sulfoselenide) accounts for 14 percent. The remainder finds use in the steel industry for improving ductility, in the rubber industry as an alternative to sulfur for vulcanization, for improving the stability of explosives, and as a fungicide in dandruff removers and agricultural chemicals. It is a necessary trace element in the diets of livestock, and livestock raised in selenium-deficient areas must have their diets supplemented.

Sources and Types of Selenium Wastes

The major sources of selenium wastes that have been identified include the following: (1) manufacture and reconditioning of xerox drums; (2) paint and pigments industry; and (3) paint residues left in containers.

The selenium and arsenic coated xerox drums are manufactured and reconditioned exclusively at Xerox's Rochester, New York facility. About 700,000 lb of solid wastes containing cotton linter, steel, aluminum, and 300 to 400 lb of selenium and arsenic are generated each year during these operations. Of the selenium and arsenic found in these wastes, there is usually more selenium present than arsenic and approximately 25 percent of the selenium is combined with arsenic chemically (e.g., arsenic triselenide), with the remaining selenium containing less than 1 percent arsenic in them. In addition, there are 50,000 lb of liquid wastes consisting primarily of caustic solutions and 0.3 percent selenium and arsenic generated each year from the same operations.

Cadmium sulfoselenide accounts for nearly all the selenium used in pigments. In the manufacture of solvent-based paints, sludges are generated from both the washing system and the solvent recovery stills. The combined solvent-based paint sludge is characterized by the following composition: 4.5 percent inorganic pigment (excluding titanium dioxide), 8.5 percent titanium dioxide, 14.5 percent pigment extenders, 25.0 percent binders and 47.5 percent organic solvents. It is estimated that a total of 370 lb of selenium are lost through 37 million lb of solvent-based paint sludges every year.*

Selenium containing paint residues left in containers normally discarded in municipal dumps constitute another source of selenium waste. It is estimated that a total of 2,560 lb of selenium are lost as paint residues every year.*

---

* The basis for these estimates are discussed in detail under "Toxic Paint Wastes" in the appendix volume on Waste Forms and Quantities.

Possible sources of trace selenium include natural fuels, leather goods, cloth materials, paper and other wood products, etc. Coal has been found with as much as 7.4 ppm Se and significant amounts have been found in newsprint. In general, materials derived from terrestrial sources have a Se/S ratio of approximately 1×10^{-4}.[1745] A comprehensive study of selenium contained in solid waste has been made.[1745] The principal means of access to the environment is by incinerator stack emission, where emissions of 0.002 mg/m^3 were found. Quench water samples showed 0.014 mg/l. These levels compare favorably with the present TLV of 0.2 mg/m^3 and drinking water recommendation of 0.01 mg/l. No information is available, however, on the seasonal and geographical variations of these emissions.

2. TOXICOLOGY

Health and Safety Standards

Commercial elemental selenium is relatively inert and is handled without special precautions.[1433,1747] The 1971 HEW Annual List of Toxic Substances[1312] does not list selenium metal as a toxic substance. The Threshold Limit Value, (TLV)[0766] as recommended by the American Conference of Governmental Industrial Hygienists in 1968 was 0.1 mg/m^3. This was recently raised to 0.2 mg/m^3.[1745] Most industrial absorption occurs by inhalation of dust, vapors, and fumes,[0277] and care therefore should be taken to scrub exhaust gases and employ good housekeeping procedures. Care should also be taken that volatile or soluble selenium compounds not be formed, since these are many times more toxic than the metal itself. Organoselenium compounds are particularly dangerous.

Epidemiology

The principal cause of selenium poisoning in the United States is the consumption of vegetables and grains grown in selenium-rich soils, particularly in the Northwest plains states. Industrial exposures are apparently rare.[0277] The common symptoms are a characteristic garlic breath, often accompanied by dermatitis, gastrointestinal disturbances, and/or damage to the lungs, liver, and other viscera.[1287,0766] Fifty to eighty percent of ingested selenium is excreted through the kidneys and a conclusive diagnosis may be obtained from urinalysis. Persons not exposed industrially to selenium average 0.01 to 0.15 mg Se/liter urine, depending on their geographical location. Industrial workers average 0.069 mg/l. It has been determined that humans can excrete 2.00 mg/l without exhibiting symptoms.

3. OTHER HAZARDS

In common with almost all metals, sufficiently fine selenium powder may explode in air to form the water-soluble SeO_2. Selenium will react with acids to form the highly toxic H_2Se gas. If another metal is present, a selenide may form, which would then react with water vapor to form H_2Se.

4. DEFINITION AND EVALUATION OF WASTE MANAGEMENT PRACTICES

Handling, Storage, and Transportation

There are no special shipping regulations for selenium metal.[0278,1747] Metal should be stored in such a way as to avoid contact with water, and fine powder should be sealed under inert gas to avoid the possibility of an explosion. A fire involving selenium can be handled as any metal fire would. An time there is a possibility of the evolution of airborne dusts or fumes or the possibility of an uptoward chemical reaction, controlled exhaust ventilation should be provided.

Disposal Reuse

At $4.50/lb for commercial grade selenium metal, the metal is an attractive candidate for secondary recovery and resale to the primary producers, and 30,000 lb/yr are recycled in this way. For the disposal of selenium wastes, the acceptable criteria is defined in terms of the recommended provisional limits:

Contaminated and Environment	Provisional Limits	Basis for Recommendation
Selenium in Air	0.002 mg/M^3	0.01 TLV
Selenium in Water and Soil	0.01 ppm (mg/l)	Drinking Water Standards

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Selenium waste may be divided into two categories, that which comes from the refining or manufacture of selenium and selenium products and that which arises incidentally from the disposal of wastes containing trace quantities of selenium.

Option No. 1 - Scrubbing with Hydrobromic Acid. Selenium refineries are typically equipped with wet scrubbers containing 40 to 48 percent HBr in aqueous solution with 5 to 10 percent free bromine added. The acid vapors are absorbed in a soda lime train, while the selenium is separated from the HBr solution by a straightforward distillation. The recovered selenium is then recycled.[0277] On an industrial level, the hazards associated with selenium are apparently handled adequately, as evidenced by the lack of disease associated with the selenium producers.

Option No. 2 - Sanitary Landfill. The selenium containing solid wastes from the manufacture and reconditioning of xerox drums are currently disposed of by burial in a segregated section of a landfill site for industrial wastes. Waste sludges containing selenium and toxic heavy metals from the manufacture of paint and pigments are also disposed of in approved sanitary landfill sites. It is felt that sanitary landfill is an acceptable and adequate method for the disposal of selenium wastes, provided that the sites used are located over nonwater-bearing sediments or have only unusable ground water underlying them and are completely protected from flooding, surface runoff or drainage, so that all waste materials and internal drainage are restricted to the site. In other words, any sanitary landfill sites approved for the disposal of selenium wastes must meet the criteria for a Class 1 disposal site in California.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Despite intensive investigations, no correlation has been found between selenium-related disease and employment in the selenium industry. Similarly, no incident disease has been attributed to air or water emissions or other wastes emanating from plant sites.

Selenium-related diseases in man and livestock have been found in certain areas of the country (e.g., the Northwest plains states), whose indigenous soils contain an unhealthily high concentration of selenium. Likewise, selenium deficiencies have induced pathologies in livestock in other areas. This is not a disposal problem, but rather a problem involving health screening of the indigenous animal and human populations and appropriate dietary recommendations. It indicates, however, that the disposal of selenium should be accomplished such that water and soil contamination with soluble selenium compounds is avoided.

Studies to date indicate that the disposal of municipal and other wastes containing trace quantities of selenium does not generally result in unsafe levels in the environment.[1745] These studies, however, were not extended to an investigation of seasonal and geographical variations. Also, while it has been determined that terrestrial mammals, including man, do not concentrate the metal,[1748] no information was found regarding the possible concentration of selenium in plants.

At this time, selenium is not considered as a candidate waste stream constituent for National Disposal Sites. However, no investigations have been conducted to determine what seasonal and geographical variations exist in the emission of trace selenium from the disposal of municipal and other wastes, and whether these variations are sufficient to cause occasional emissions at an unsafe level. Furthermore, the ability of plants and animals to assimilate and concentrate selenium has not been investigated to determine if unsafe levels can be attained in this way.

If it is determined that a combination of circumstances can lead to unsafe levels, intermittent or permanent controls will have to be imposed on the time and place of disposal and the content of general wastes (e.g., newsprint and other paper) now disposed of without regard of their selenium content. In this eventuality, National Disposal Sites might prove economical for the disposal or recycling of these wastes.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name

IUC Name Selenium Powder (367)

Common Names Selenium Powder

Structural Formula

Se (solid)
Se_8 (liquid)
Se_x (gas) with
$< 1 \ x \leq 8$

Molecular Wt. 78.96 Melting Pt. 217 C Boiling Pt. 685 C

Density (Condensed) 4.82 @ 25 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C) $\log P_{mm} = 8.0886-4989.5/T(K)$

1 mm @ 356 @ @

Flash Point N.A. Autoignition Temp. N.A.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Hot Water Ethanol

Others: H_2SO_4, HNO_3, CS_2

Acid, Base Properties Weakly acidic

Highly Reactive with Acids to form toxic H_2Se gas; may react similarly with water or water vapor; finely divided powder may explode

Compatible with steel, plastic

Shipped in steel drums (may be plastic-lined for ultimate purity)

ICC Classification None Coast Guard Classification

Comments

PROFILE REPORT

Sodium Acid Sulfite (380), Sodium Nitrite (397), Sodium Sulfite (405)

1. GENERAL

Introduction

The inorganic chemicals in this report are basically nontoxic. However, when dissolved in water in sufficiently large quantities they may create a hazard or nuisance. They are grouped together here in one report because they can be handled by similar disposal processes.

Manufacture and Uses

Sodium Acid Sulfite. Sodium acid sulfite, $NaHSO_3$, is prepared as white crystals or as crystalline powder that has a slight sulfurous odor and a disagreeable taste. It is prepared by saturating sodium carbonate solution with sulfur dioxide gas. The product is obtained as a suspension which is removed from the solution by centrifuging. The dried product is really the sodium metabisulfite, $Na_2S_2O_5$, which yields $NaHSO_3$ upon solution in water. It finds industrial use either as a solution or as a solid. The solutions may be shipped, stored and handled in lead-lined equipment. In the tanning industry sodium acid sulfite is used as a reducing agent for chrome solutions. In the textile industry it is a bleaching agent, a dechlorinating agent, and a raw material for the manufacture of hydrosulfite solutions. It is also consumed in the paper, photographic and organic chemical industries.[1416,1662]

Sodium Nitrite. Sodium nitrite, $NaNO_2$, is prepared as slightly yellowish or white crystals, pellets, sticks or powder that oxidizes upon exposure to air. In the dye industry sodium nitrite is a very important chemical, used for the diazotization of amines for making azo dyes. It is also used in the preparation of nitric oxide, pickling metal, medicine, rustproofing and cutting oils. Formerly sodium nitrite was prepared by the reaction,

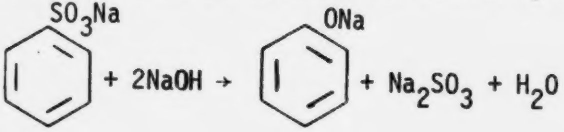
$$NaNO_3 + Pb \rightarrow NaNO_2 + PbO.$$

Now it is manufactured by passing NO, obtained by oxidation of ammonia, into soda ash solution.

$$Na_2CO_3 + 2NO + 1/2O_2 \rightarrow 2\ NaNO_2 + CO_2$$

Sodium nitrate is also formed and is separated from sodium nitrite by crystallization in lead lined equipment.[1416,1662]

Sodium Sulfite. Sodium sulfite, Na_2SO_3, is manufactured as white crystals or powder. It is a compound that is easily oxidized. For this reason it is employed in many cases where a gentle reducing agent is desired. It is employed to bleach wool, silk and as an "antichlor" (dechlorinating agent) after bleaching of yarns, textiles, and paper, as a preservative for foodstuff and to prevent raw sugar solutions from coloring upon evaporation. It is also used in photography, medicine and to remove oxygen from boiler water. The most important commercial manufacturing process starts by passing sulfur dioxide into a solution of soda ash until the product is acid. Then sodium sulfite is formed by adding the stoichiometric quantity of soda ash, and boiling until carbon dioxide is evolved. After the carbon dioxide has been evolved, the solution is concentrated, whereupon the crystals of $Na_2SO_3 \cdot 7H_2O$ settle out upon cooling. Another commercial source of sodium sulfite is as a byproduct from the preparation of phenol by the fusion of sodium benzene sulfonate with sodium hydroxide.



Sodium sulfite is also recovered from paper mill cellulose waste liquors.[0955, 1416,1662]

Physical and Chemical Properties

The physical and chemical properties of the inorganic chemicals treated in this report are summarized on the attached worksheets.

2. TOXICITY

The materials treated in this report are not highly toxic. However, they are all soluble in water to yield solutions that are corrosive and in high concentrations are irritating to the skin and mucous membranes. Two of the compounds, sodium nitrite and sodium sulfite, are employed as food additives. No Threshold Limit Values (TLV's) have been recommended by the American Conference of Governmental Industrial Hygienists for these compounds.[0225] Sodium nitrite has a lethal dose reported as "or LD_{50} 480 mg/Kg rat".

3. OTHER HAZARDS

The three compounds covered by this report are generally considered to be reducing agents. Sodium nitrite, however, is also an oxidizing material that is a fire hazard when in contact with organic or other easily oxidized material. All three compounds are corrosive to most metals and require lead-lined equipment for storage of concentrated solutions.[0955]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

The three materials covered by this report may be handled and stored as strong solutions in lead-lined equipment. Sodium acid sulfite must be protected from air to avoid oxidation. Sodium nitrite is classified by the Department of Transportation (DOT) and the U. S. Coast Guard as oxidizing material that required a Yellow Label.[0766] The other materials do not have shipping regulations.

Disposal/Reuse

Industrially contaminated materials covered in this report, when in sufficient quantity, can be reprocessed for reuse. Usually the materials can be purified by recrystallization. The safe disposal of these materials are defined in terms of the recommended provisional limits in the atmosphere and in water and soil environments. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Sodium Bisulfite	0.02* mg/M^3	0.01 TLV*
Sodium Nitrite	0.02* mg/M^3	0.01 TLV*
Sodium Sulfite	0.02* mg/M^3	0.01 TLV*

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Sodium Bisulfite	0.10* mg/l	Stokinger and Woodward Method
Sodium Nitrite	0.10* mg/l	Stokinger and Woodward Method
Sodium Sulfite	0.10* mg/l	Stokinger and Woodward Method

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*Estimated

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The disposal of the reducing agents covered by this report is accomplished by diluting the materials with a large volume of water containing soda ash and then adding calcium hypochlorite. The solution is decanted or siphoned into another container if sulfate is present. The solution is then neutralized with 6M-HCl, diluted and discharged into a sewer or stream. The sludge, if any, is added to a Class 2 type landfill. This method is considered satisfactory for the three materials covered by this report.[0095]

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The chemical compounds discussed here have been classified on a preliminary basis as probable candidate waste stream constituents for municipal disposal. Based on the disposal process described in Section 5, it may be concluded that waste treatment for these compounds can be handled adequately locally and no consideration for treatment at National Disposal Sites is warranted.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sodium acid sulfite (380)

IUC Name Sodium acid sulfite

Common Names Sodium bisulfite

Structural Formula

$NaHSO_3$

Molecular Wt. 190.11(1) Melting Pt. decomposition(1) Boiling Pt.

Density (Condensed) 1.48g/cc @ 20 C(1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water very soluble(1) Hot Water very soluble(1) Ethanol slightly soluble(1)

Others:

Acid, Base Properties

Highly Reactive with ozidizing materials

Compatible with

Shipped in 500 lb barrels; 500-, 600-lb drums; solution in 500-lb barrels(2)

ICC Classification none(2) Coast Guard Classification None(2)

Comments When dried sodium metabisulfite, $Na_2S_2O_5$, is formed(2)

References (1) 1570
(2) 1416

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sodium nitrite (397)

IUC Name

Common Names Diazotizing salt

Structural Formula

$NaNO_2$

Molecular Wt. 69.01(1) Melting Pt. 271 C(1) Boiling Pt. 320 decomp(1)

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 72g/100 g at 0 C(1) Hot Water 163g/100g at 100 C(1) Ethanol slightly soluble(2)

Others: 0.3g/100 g ether at 20 C(1)

Acid, Base Properties

Highly Reactive with Reducing or oxidizing materials(2)

Compatible with

Shipped in 25-, 100-lb drums; 150-lb kegs; 400-lb barrels(2)

ICC Classification oxidizing material(2) Coast Guard Classification oxidizing material(2)

Comments

References (1) 1570

(2) 1416

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sodium sulfite (405)

IUC Name Sodium sulfite

Common Names

Structural Formula

Na_2SO_3

Molecular Wt. 126.05(1) Melting Pt. decomposes Boiling Pt.

Density (Condensed) 2.633g/cc @ 15.4 C(1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 12.54g/100 ml at 0 C(1) Hot Water 28.3g/100 ml at 80 C(1) Ethanol Slightly soluble(1)

Others:

Acid, Base Properties

Highly Reactive with Oxidizing materials

Compatible with

Shipped in 100-,200-lb bags; 234-, 450-lb barrels; 400-lb drums(2)

ICC Classification None(2) Coast Guard Classification None(2)

Comments

References (1) 1570

(2) 1416

PROFILE REPORT

Sodium Alloy (374) and Sodium-Potassium Alloy (402)

1. GENERAL

Chemical Profiles[0767] and contacts with the Ethyl Corporation[0595] indicate that sodium is produced at five plants in the United States: two DuPont plants at Niagara Falls, New York, and Memphis, Tennessee, two Ethyl plants at Baton Rouge, Louisiana and Houston, Texas, and a Reactive Metals plant at Ashtabula, Ohio. Total annual production is 180,000 tons of which 90 percent is used in the production of tetraethyl lead with no associated waste metal or metal oxide. If or when tetraethyl lead production ceases in 1975, Ethyl estimates that Na production will shrink to 15 to 30,000 tons/year and four of the five plants will probably close.

Kirk-Othmer[1433] reports that all of the Na production in the United States is by the Downs process. A representative at the Ethyl Corporation plant in Baton Rouge, Louisiana estimates that his waste amounts to about 1 percent of his total Na production and is in the form of a sludge containing Na, Ca, CaO, and Na_2O. This translates to a generated waste of about 3,000 lb sludge/day. This sludge is drummed and dumped at sea with perforations to assure complete reaction and destruction. The DuPont plant at Niagara Falls, New York [0596,0664] generates waste of 100 lb Na/day for a plant of similar size. This material is mixed with kerosene and burned in a closed reactor. The exhaust gases are scrubbed with water and sewered.

The use of sodium as a coolant and heat transfer medium in nuclear reactors has declined in recent years, but the Atomic Energy Commission[0593] expects that it may again become important as fast breeder reactors become onstream around 1980. It is impossible to judge the magnitude of this use at this time, because it will be affected by many policy decisions to be made between now and then. In this event, they envision closed loop purification processes, perhaps similar to that invented by the De Vries and Scarborough.[0464] Their invention purifies Na or NaK in a continuous process by taking advantage of the virtual insolubility of Na_2O just above the melting point (97.9 C). The material is heated or cooled to the appropriate temperature; the pure metal is pumped from the bottom and the less dense impure metal oxides are skimmed from the top.

The Sodium Reactor Experiment at Atomics International, Canoga Park, California[0398,0399] inventories about 100,000 lb of Na, of which about 30,000 lb is disposed of as waste every year by dumping at sea.

There are two commercial uses for potassium in the United States -- as a component of NaK for catalysis and cooling systems and for the production of K_2O_2 for use in breathing apparatus. Total potassium production is 100 tons/year by a sole supplier, MSA,[0395] and is expected to remain constant over the next 10 years. Kirk-Othmer[1433] reports the production processes to be:

$$\text{Na} + \text{KCl} \longrightarrow \text{NaK} + (\text{Na,K})\ \text{CL} \xrightarrow{\text{distillation}} \text{K}$$

The waste products from the NaK and K production are the oxides and chlorides of sodium and potassium. MSA would not release any waste production figures, but did say the oxides are neutralized in settling ponds and then discharged into nearby rivers. The mixed chloride salts are trucked to a nearby abandoned mine. The largest NaK customer in the United States is the Union Carbide Corporation, Charleston, West Virginia.[0665]

2. TOXICOLOGY

The materials are not toxic in a strict sense, but are dangerous because of their caustic properties. The oxides or hydroxides are formed vigorously on contact with air or moisture or human tissue. The reported Threshold Limit Value (TLV) for sodium hydroxide is 2 mg/M^3, as recommended by the ACGIH. The hydroxides themselves are caustic in concentrated form, but neutralization with acids, such as hydrochloric acid, eliminates this hazard.

3. OTHER HAZARDS

Na and NaK are spontaneously flammable in contact with moisture to evolve H_2 with sufficient heat to ignite the H_2. They ignite spontaneously in Cl_2 and react vigorously with moisture, acids, and human tissues.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Procedures for adequate handling, storage, and transportation of these materials are well documented by the Manufacturing Chemists Association,[0765] the Liquid Metals Handbook,[0463] and the Liquid Metals Handbook - Na Supplement.[0463]

Disposal/Reuse

The safe disposal of wastes containing sodium and sodium-potassium alloys is defined in terms of the recommended provisional limits:

Contaminant in Air	Provisional Limits	Basis for Recommendation
Sodium	0.02 mg/M^3 as NaOH	Provisional limit for NaOH
Sodium-potassium alloy	0.02 mg/M^3 as NaOH and KOH	Provisional limits for NaOH and KOH

Contaminant in Water or Soil	Provisional Limits	Basis for Recommendation
Sodium	0.1 ppm as NaOH	Provisional limit for NaOH
Sodium-potassium alloy	0.1 ppm as NaOH and KOH	Provisional limits for NaOH and KOH

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Primary Na producers either drum their waste and dump it at sea with perforation in the drums to assure complete reaction and destruction (Ethyl Corporation, Baton Rouge, Louisiana)[0595] or burn it mixed with kerosene in a closed chemical reactor (DuPont Corporation, Niagara Falls, New York).[0596,0664] The use of a reactor allows the burning to be controlled by varying the feed rates of sodium and air to prevent a violent conflagration and also allows the exhaust gases to be scrubbed with water to remove the sodium oxide and carbonate.

The 30,000 lb/year of Na waste produced by Atomics International is packed in barrels on site. The California Salvage Company[0400] picks up this material under contract, fits the barrels with concrete collars and dumps them at sea off Santa Catalina Island. The cost of this service is $2,200 on an annual basis. This method of disposal is currently considered satisfactory to all parties concerned, including the California Water Quality Control Board[0384] and the California Department of Fish and Game.[0401]

NaK and K_2O_2 production by MSA at their single location in Evans City, Pennsylvania is reported to be under control.[0395] No toxic materials are generated by the production of these materials and the hydroxide effluent is neutralized in settling ponds to whatever pH is acceptable. The (Na,K) Cl waste is a neutral salt and deposition in an abandoned mine poses no problems. As the sole supplier of 100 tons K/year with NaK selling for $1.55/lb in 200 lb barrels, the economics of these disposal processes certainly aren't constricting.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The disposal processes for sodium and sodium-potassium alloys are currently adequate at the industrial level, and these materials should not be considered as candidate waste stream constituents for national disposal.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name

IUC Name SODIUM (374)

Common Names SODIUM

Structural Formula

Na

Molecular Wt. 23.0 Melting Pt. 97.9 C Boiling Pt. 892 C

Density (Condensed) 0.971 @ 20 C Density (gas) 0.003 @ 900 C

0.040 @ 1800 C

Vapor Pressure (recommended 55 C and 20 C)

1.2 mm @ 400 C @ @

Flash Point Autoignition Temp. 115 C

Flammability Limits in Air (wt %) Lower Dangerous Upper

Explosive Limits in Air (wt. %) Lower Dangerous Upper

Solubility

Cold Water Reacts to form NaOH + H_2 Hot Water reacts Ethanol reacts

Others: Reacts with $NH_3 \rightarrow NaNH_2 + 1/2\ H_2$

Acid, Base Properties strongly basic

Highly Reactive with Moisture, human tissue, spontaneously flammable in air, evolves H_2 and heat, ignites in Cl_2, CS_2, $POCl_3$, acids

Compatible with metals

Shipped in Pumped in and out of tank cars molten; shipped under N_2

ICC Classification Flammable solid, yellow label, 25 lb Coast Guard Classification Flam. solid, yellow label

Comments Sec. 73.206

for 1155-1735 K: log P (atm) = 6.67176-5544.97/T-0.61344 log T

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name

IUC Name SODIUM-POTASSIUM ALLOY (402)

Common Names NaK

Structural Formula

NaK

Molecular Wt. 77%K, 23%Na   Melting Pt. -12.5 C   Boiling Pt. 1446 F

Density (Condensed) 0.732 g/ml @ 950 F   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

0.46 psia@ 950 F   @   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower dangerous   Upper

Explosive Limits in Air (wt. %)   Lower dangerous   Upper

Solubility

Cold Water Reacts to evolve H_2 Hot Water reacts   Ethanol reacts

Others: NH_3(aq.)

Acid, Base Properties strongly basic

Highly Reactive with moisture, human tissure, spontaneously flammable in air, evolves H_2 and heat

Compatible with metals

Shipped in under inert gas in steel containers with valves and downpipes

ICC Classification flam. solid, yellow label, 25 lb   Coast Guard Classification

Comments Sec. 73.206

Forms explosive mixtures with chlorinated hydrocarbons

PROFILE REPORT

Sodium Azide (378)

1. GENERAL

Sodium azide, NaN_3, is a colorless crystalline substance described as being highly toxic.[0766]

Sodium azide is prepared from sodium amide and nitrogen monoxide according to the following reaction[1492]:

$$2NaNH_2 + N_2O \rightarrow NaN_3 + NaOH + NH_3$$

Fairmont Chemical Company in Newark, New Jersey is the only manufacturer of sodium azide in the United States. Last year they produced about 500,000 lb of the chemical for domestic use.[2024]

Sodium azide is used mainly as a reactant in the production of lead, silver, antimony, and mercury azides. It also has a medical use in treating hypertensive encephalopathy and other conditions which demand immediate lowering of blood pressure (dose 0.2 to 4.0 micrograms/kg body weight/minute intravenous).[1492]

The sources of sodium azide wastes may include the following: (1) sodium azide manufacturers; (2) sodium azide wholesalers; (3) manufacturers that use sodium azide as a reactant in their production process. However, DuPont claims that in their process for making lead azide, sodium azide does not appear in the waste stream.[2025] This is because there is essentially a 100 percent conversion of sodium azide to lead azide in the reaction process.

The physical and chemical properties of sodium azide are summarized in the attached worksheet.

2. TOXICOLOGY

The toxicity of sodium azide is due to the azide group (-NNN). Much of the knowledge of azide toxicity has been gained from industrial exposures and laboratory studies involving hydrazoic acid, HN_3. Dilute aqueous solutions and hydrazoic acid vapors from azide reactions have caused noticeable and measurable effects in industrial and laboratory workers.

Hydrazoic acid is easily adsorbed into the bloodstream after inhalation of the vapor or spray. The chief physiological effect is a marked lowering of the blood pressure with an accompanying rise in heart beat and an increase in the respiration rate. Eye and nose irritation, headache, weakness, and unsteadiness have also been reported following continued industrial exposures. Recovery from these effects is rapid and low level (less than 4 ppm) exposures which cause these symptoms do not appear to produce any permanent abnormal conditions.[2026]

The estimated oral LD_{50} value to the rat for sodium azide is 46 mg/kg of body weight.[1312] The 48-hour Median Tolerance Limit (TL_m) of sodium azide for bluegills is 980 micrograms/liter as established by the Federal Water Pollution Control Administration,[0536] and is indicative of the water pollution hazard associated with sodium azide.

3. OTHER HAZARDS

The explosive hazard of sodium azide is moderate when shocked or exposed to heat. However, the explosiveness of sodium azide increases somewhat when it is contaminated with certain materials. When heated to decomposition in air, sodium azide emits toxic fumes of nitrogen oxides.[0766]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Care should be exercised in handling sodium azide because of the high toxicity and explosive nature of the compound. The use of leather gloves, a heavy face shield, and a laboratory coat is recommended in handling the material. It is advisable to work behind a barricade (body shield or wall). Avoid unnecessary heat, friction or impact.[0095]

Sodium azide should be stored in a warehouse in metal containers.[2024] It should be stored away from foodstuffs, feeds, or any other material intended for human or animal consumption.

Sodium azide must be transported in wooden boxes with inside containers which are securely closed paper bags, placed within a waterproof duplex bag. The net weight of material in one outside box should not be over 100 lb.[0278] There must be a "Poison B" label on every box.

Disposal/Reuse

Fairmont Chemical Company has a policy of accepting excess amounts of sodium azide and contaminated sodium azide for reprocessing.[2024]

In the laboratory, small quantities of waste azide solutions can be discharged into the sink if adequate cold water dilution is provided. The safe disposal of sodium azide is defined in terms of the recommended provisional limits.[2026]

Contaminant and Environment	Provisional Limit	Basis for Recommendation
Sodium Azide in air	0.02 mg/m^3	Provisional limit for NaOH
Sodium Azide in water and soil	0.1 mg/l	Provisional limit for NaOH

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Concentrated Wastes

Option No.1 - Reprocessing/Disposal. Fairmont Chemical Company, the only major producer of sodium azide in the United States has indicated its willingness to accept excessive or waste sodium azide for reprocessing, purification or disposal. The details of the reprocessing technique were not revealed. Fairmont Chemical's method for disposal of sodium azide is to react it with sulfuric acid solution and sodium nitrate in a hard rubber or teflon vessel.[1236] Nitrogen dioxide is generated by this reaction and the gas is run through a scrubber before it is released to the atmosphere. It is conceivable that any industry that handles sodium azide in significant amounts would probably have facilities for reacting the sodium azide and treating the evolved nitrogen dioxide gas.

Option No.2 - Incineration. The complete and controlled oxidation of sodium azide in air or oxygen with adequate scrubbing and ash disposal is possible if the sodium azide is mixed with other combustible wastes. Since the combustion process produces nitrogen and sodium oxides, an adequate gas clean-up system must be installed to alleviate the air pollution problem.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Considering the small production and consumption of sodium azide, as well as provisions for return of waste sodium azide to the producer, it is felt that sodium azide is not a candidate waste stream constituent for national disposal. The high cost of sodium azide is in itself an incentive to the manufacturers that use the compound to minimize the amount of waste material. The simple method of disposing of sodium azide by reaction with sulfuric acid and sodium nitrate can easily be performed by any firm that handles the compound. In summary, processes for the exclusive treatment of wastes containing sodium azide are not recommended for inclusion in the National Disposal Site scheme.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sodium Azide (378)

IUC Name ____________

Common Names Sodium Azide

Structural Formula

NaN_3

Molecular Wt. 65.02   Melting Pt. decomposes   Boiling Pt. decomposes in a vacuum

Density (Condensed) 1.846 @ 20 ____   Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____   ____ @ ____   ____ @ ____

Flash Point ____   Autoignition Temp. ____

Flammability Limits in Air (wt %)   Lower ____   Upper ____

Explosive Limits in Air (wt. %)   Lower ____   Upper ____

Solubility

Cold Water 41.7g/100cc @ 17 C   Hot Water ____   Ethanol 0.314/100cc @ 16 C

Others: ____

Acid, Base Properties ____

Highly Reactive with ____

Compatible with ____

Shipped in ____

ICC Classification Poison B   Coast Guard Classification Poison B

Comments Shock will explode it; when heated to decomposition, it emits toxic fumes of nitrogen oxides, and may explode.

References (1) 0766

PROFILE REPORT

Sodium Chlorate (385)

1. GENERAL

Introduction

Sodium chlorate, $NaClO_3$, is a white crystalline solid which is slightly hygroscopic. The compound is a soluble oxidizing agent in acid and neutral solutions, but in basic solutions at room temperature it does not show oxidizing properties.

In acid solutions, sodium chlorate is a source of chloric acid, a powerful oxidizing agent. Chlorates are strong oxidizers, comparable to manganese materials and chlorine. They are stronger than bromates or iodates. The molten salt is also a powerful oxidizing agent.[2122]

In 1969, there were 187,125 tons of sodium chlorate produced in the United States. In 1970, the production was 221,000 tons and the projected annual demand for sodium chlorate by 1974 is 265,000 tons.[1596]

Manufacture

All of the chlorate produced in the United States is prepared by electrolysis of a solution of chloride and chlorate in a diaphragmless cell.[1433]

A number of reactions take place at the anode. Chlorine is liberated and reacts with hydroxide ion to produce hypochlorite and chloride ions, and with water to form hypochlorous and hypdrochloric acid:

$$2\ Cl^- \longrightarrow Cl_2 + 2e^-$$

$$Cl_2 + 2OH^- \longrightarrow ClO^- + Cl^- + H_2O$$

$$Cl_2 + H_2O \longrightarrow HClO + H^+\ Cl^-$$

By maintaining the electrolyte at pH 6.2 to 7, favorable conditions for the reaction between hypochlorous acid and hypochlorite ions can be maintained, so that chlorate is formed. This is a slow reaction, and takes place in the body of the cell rather than at or near the anodes.

The reactions for the electrolyses of sodium chloride, and for the formation of hypochlorus acid and hypochlorite ion from the evolved chlorine, may be combined with the reaction for the hypochlorous acid-hypochlorite ion to form chlorate, giving the overall reaction:

$$NaCl + 3H_2O \longrightarrow NaClO_3 + 3H_2$$

Six faradays are required per mole of sodium chlorate formed; the overall reaction is 100 percent efficient.[1433]

Large scale commercial facilities for the manufacture of sodium chlorate include the following[1506]:

Kerr-McGee Chemical Corporation; Hamilton, Mississippi and Henderson, Nevada

Hooker Chemical Corporation; Columbus, Mississippi

Penn-Olin Chemicals; Calvert City, Kentucky.

Uses

Sodium chlorate is used extensively as a source of chlorine dioxide for paper pulp bleaching. It is used in tanning and finishing leather, in processing of furs, in the preparation of dyes, as a mordant in textile dyeing and printing, for production of bromine from brines, for medicinal purposes, in metallurgy operations, processing of uranium ore, and as an intermediate in the production of perchlorates. In agriculture, it is used as a cotton and tomato defoliant, and it is used as a weed killer. Battery-active manganese dioxide can be made by a chemical process using sodium chlorate oxidation of manganese. It is also a selective oxidizing agent in organic synthesis.[2122]

Sources and Types of Sodium Chlorate Wastes

The sources of sodium chlorate wastes may include the following: (1) sodium chlorate manufacturers, (2) agricultural users, (3) government facilities that store, transport, and use sodium chlorate, and (4) commercial and industrial processes including those from paper manufacturers, textile dyeing and printing operations, metallurgy operations, etc.

In general, most of the sodium chlorate waste will be in concentrated form as a result of spills occuring in the transporting and handling of the materials or as a partially degraded or contaminated surplus material. For example, the U. S. Army currently has 12,000 lb of sodium chlorate-borate mixture stored in Pennsylvania awaiting disposal. The electrolytic process used in manufacturing sodium chlorate is a closed process and no waste is generated other than accidental spills or the small amount of chlorate, mixed with other solids, which is left as residue after the filtering process. In the bleaching process (in paper manufacturing) there is essentially a 100 percent conversion of sodium chlorate to chlorine dioxide, so that there is no waste chlorate other than spills involved in handling the material.[2120]

Dilute sodium chlorate wastes include those generated in agricultural runoffs and possible spent solutions used to clean empty containers.

Physical and Chemical Properties

The physical and chemical properties of sodium chlorate are included in the attached worksheet.

2. TOXICOLOGY

Sodium chlorate is not highly toxic, but ingestion or excessive inhalation of dust should be avoided. Ingestion of relatively large quantities (15-30 gm) of the material may prove fatal. Abdominal pain, nausea and vomiting, diarrhea, pallor, blueness, shortness of breath, unconsciousness and collapse are the immediate symptoms following ingestion of toxic amounts of sodium chlorate. Prolonged exposure to sodium chlorate dust may cause skin irritation to the mucous membranes of the eyes, nose and throat.[2123]

The intraperitoneal LD_{50} value of sodium chlorate to the mouse is 550 mg/kg of body weight.[1312]

3. OTHER HAZARDS

Sodium chlorate is a strong oxidizing agent and constitutes an extreme fire and explosion hazard if allowed to come in contact with organic or combustible materials, acids, or reducing substances.

Dry materials such as wood, clothing, paper, and leather contaminated with sodium chlorate may easily be ignited by friction, percussion, or any source of heat such as flames, sparks, welding torches, lighted cigarettes, and hot surfaces. Ignition can also occur when sodium chlorate dust comes in contact with clothing that is damp with perspiration and which then dries.[2124]

Mixtures of sodium chlorate with oxidizable organic substances such as oils, greases, waxes, solvents, paints, sugars, alcohols, wood dust, lint, and vegetable dusts are potential fire and explosion hazards.

Certain easily oxidizable or finely divided inorganic materials such as ammonium compounds, sulfur and its compounds, sulfides, phosphorous, powdered metals, and metal salts (especially copper) are potential fire and explosion hazards when mixed with sodium chlorate.[2124]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transporation

In handling chlorates, workers should wear clean coveralls daily, as well as washable rubberized gloves, boots or shoes. A washable head covering should also be used. In dusty conditions, goggles and an approved dust respirator should be used. Use of leather shoes or gloves is not recommended because when contaminated it may not be possible to remove completely all traces of chlorate from the leather. Workers should avoid using oils, greases or protective creams on skin, as flammable mixtures may develop on prolonged contact of these materials with chlorates.[2123]

Dry bulk sodium chlorate should be stored in lined steel, concrete or tight glazed tile silos or tanks. Dessicated air should be supplied to prevent caking from atmospheric moisture. Storage of sodium chlorate in drums should be in a cool, dry, fireproof building. Dry concrete floors are preferable to wooden decks. Spillage should be swept up and removed at once. Sodium chlorate solutions or slurries may be stored in steel-lined tanks.[2123]

Sodium chlorate is shipped in metal drums (returnable and single trip) and in tank cars. It is classified by the Department of Transportation (DOT) as an oxidizing material and must be packed in DOT specification containers when shipped by rail, water or highway. All of the DOT regulations regarding loading, handling, and labeling must be followed.[2123]

Disposal/Reuse

Contaminated or degraded sodium chlorate is not currently reprocessed. Contaminated sodium chlorate is disposed of by one of the methods described in Section 5.

Although sodium chlorate is very soluble in water, it does not appear to be a serious water pollution problem. The small amount of sodium chlorate that is discharged into sewers, lakes, or streams will readily supply oxygen to the BOD or COD present in the water and be reduced to the chloride ion. Chlorate ion will be rapidly reduced to the chloride ion by any reducing agent present in the water.[2120]

For the safe disposal of sodium chlorate, the acceptable criteria for its release into the environment are defined in terms of the following provisional limits:

Contaminant and Environment	Provisional Limit	Basis for Recommendation
Sodium chlorate in air	0.02 mg/M^3	Provisional limit for NaOH
Sodium chlorate in water and soil	0.10 ppm (mg/l)	Provisional limit for NaOH

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Reduction

The most acceptable method for disposing of both solid and aqueous sodium chlorate waste is to reduce it with a reducing agent in a plastic vessel. If the waste is present in the solid form, it is first dissolved and then reduced in the vessel. The most economical and readily available reducing agent is iron filings. Pickle liquor from the iron and steel industry is also a good reducing agent. The sodium chlorate is reduced to sodium chloride in the reduction process and the resulting iron precipitate can be removed with a lime slurry, soda ash, or sodium hydroxide followed by a lagooning operation.[2121]

Option No. 2 - Incineration

A small amount of sodium chlorate waste can be incinerated if it is mixed with a large quantity of other combustible waste. An adequate gas clean up to remove the gaseous combustion products must be installed to alleviate the air pollution problems.[2121]

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Considering the small amount of waste sodium chlorate present in industry and the lack of a water pollution problem associated with the compound, it is felt that sodium chlorate waste streams do not warrant National Disposal Site treatment. The simple method of disposing of sodium chlorate by reduction with ferrous ion can easily be performed by a firm that handles the compound. In summary, processes for the exclusive treatment of sodium chlorate are not recommended for inclusion in the National Disposal Site scheme.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sodium Chlorate (385)

IUC Name

Common Names Sodium Chlorate

Structural Formula

$NaClO_3$

Molecular Wt. 106.45 Melting Pt. 248 C Boiling Pt. Decomposes @ 300C

Density (Condensed) 2.490 @ 15 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 79 g/100 g @ 0C Hot Water 140g/100 g @50 C Ethanol

Others:

Acid, Base Properties

Highly Reactive with organic substances, solvents, oils, sulfur sulfides, phosphorous, powdere metals and ammonium salts.

Compatible with Sulfates, carbonates, nitrates and oxides.

Shipped in metal drums (returnable and single trip), tank cars.

ICC Classification oxidizing material, yellow label Coast Guard Classification oxidizing material, yellow label

Comments

References (1) 0766.

PROFILE REPORT

Sodium Iodide (395)

1. GENERAL

Introduction

Sodium iodide, NaI, is a white, deliquescent crystalline solid. Sodium iodide is prepared by treating ferroso-ferric iodide (see discussion in Section 5) with sodium carbonate. Iron hydroxide is removed from the reaction product by filtration. The filtrate, which contains the sodium iodide in solution, is concentrated and the sodium iodide recovered by crystallization. Sodium iodide is used in photography, medicine, analytical chemistry, and (in solution) as a solvent for iodine.[1492,1662]

Physical/Chemical Properties

The physical/chemical properties of sodium iodide are summarized in the attached worksheet.

2. TOXICITY

Sodium iodide is generally nontoxic, unless an overdose is ingested.

3. OTHER HAZARDS

Sodium iodide becomes dark if exposed to light due to the liberation of molecular iodine. The toxicity reactivity and corrosive characteristics are sharply due to the free iodine present.

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4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

Sodium iodide should be protected from moisture and light. There are no other special handling or storage requirements. Sodium iodide is shipped in 25-, 100-, and 300-lb drums. There are no Department of Transportation (DOT) shipping regulations covering this material.[1492]

Disposal/Reuse

Because of economic considerations, iodides are usually recovered for reuse. The methods for recovery are discussed in Section 5. The safe disposal of NaI is defined in terms of the recommended provisional limits in the atmosphere and in water and soil environments. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Sodium Iodide	0.02 mg/M^3*	0.01 TLV
Contaminant in Water and Soil	**Provisional Limit**	**Basis for Recommendation**
Sodium Iodide	0.10 mg/l*	Stokinger & Woodward Method

*Estimated

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Iodine can be recovered from concentrated sodium iodide wastes or waste streams by the processes used to recover iodine from brines. The processes used are discussed in the following paragraphs as Options No.1 and No.2.

Option No. 1 - Silver Iodide Process

Sodium iodide in dilute aqueous solution (either as a waste stream or from off-specification sodium iodide) is reacted with a 2 percent silver nitrate solution in the presence of ferric chloride solution as a coagulant. A wood tub is usually used. The mixed $AgI\text{-}Fe(OH)_3$ precipitate produced by the reaction settles and is treated with concentrated hydrochloric acid to dissolve the iron hydroxide precipitate. Iron scrap is added, forming ferrous iodide and silver metal, the reaction being completed within an hour. The silver is removed by filtration and converted to silver nitrate. The ferrous iodide solution is treated with an oxidant such as chlorine to precipitate the iodine. The iodine is separated and melted under concentrated sulfuric acid; the purified iodine is taken off, freed of residual H_2SO_4 and packaged.[1662]

Option No. 2 - Blow Out Process

A dilute solution containing sodium iodide is acidified with sulfuric acid to a pH under 3.5. The acidified brine is chlorinated and stripped in an acidproof brick-lined blowing-out tower, by passage through the tower countercurrent to a stream of air. The iodine-laden airstream is then passed through an absorbing tower countercurrent to recirculating dilute sulfuric acid. Sulfur dioxide is added to the sulfuric acid effluent from the tower to reduce the free iodine:

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$$

The iodine is reprecipitated by chlorinating the $HI\text{-}H_2SO_4$ liquor. The precipitated iodine is filtered, dried with concentrated sulfuric acid, and heated to melt the iodine, which is taken off, freed of residual H_2SO_4, and packaged. This process is in operation in the California oil fields and is a continuous process.[1662] Waste sodium iodide can be sent to plants operating this process, but the process cannot be used economically to treat small batches of sodium iodide.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Sodium iodide wastes can be treated at plants recovering iodine from brines using the processes described in Options No. 1 and 2, or small quantities of sodium iodide contaminated wastes can be accumulated at National Disposal Sites and sold to iodine recovery plant operators for recovery via Options 1 or 2. Because of the value of iodine, it is not anticipated that sodium iodide will be sent to National Disposal Sites, but it is anticipated that most wastes will be treated at existing iodine recovery plants or at the point of origin by Option No. 1.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sodium Iodide (395)

IUC Name

Common Names

Structural Formula

NaI

Molecular Wt. 149.92 Melting Pt. 651 C(1) Boiling Pt. 1300 C(1)

Density (Condensed) 3.667g/cc @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 158.7g/100 ml at 0 C Hot Water 256.8g/100 ml at 100 C Ethanol slightly soluble

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in Drums (2)

ICC Classification None(2) Coast Guard Classification None(2)

Comments

References (1) 1570

(2) 1492

PROFILE REPORT

Sodium Silicates (403)

1. GENERAL

Introduction

The sodium silicates, $Na_2O \cdot X\ Si\ O_2 (X = 2,3,4,5)$, are made by fusing sodium carbonate and silica (sand) in a furnace resembling that used for the manufacture of glass. The reaction that takes place at 1,300 C is as follows:

$$Na_2CO_3 + X\ SiO_2 \overset{\Delta}{\rightarrow} Na_2\ O \cdot X\ SiO_2 + CO_2$$

The most common commercial silicates are those where X equals 2.0 and 3.2. The product upon cooling forms a clear light bluish-green glass. To make sodium silicate solutions, the product is ground and dissolved in water in a steam injected, pressurized reactor. Alternatively, the melt from the furnace is passed directly without chilling into an open rotary dissolver where solution is effected at atmospheric pressure.

The silicates as 32 to 47 percent solutions find considerable use as adhesives for many kinds of materials, especially plywood and paperboard for corrugated containers. Water glass solutions are also used in detergents, metal cleaning, fireproofing and sizing.[0095,1662]

Physical/Chemical Properties

The chemical/physical properties of the silicates are summarized in the attached worksheet.

2. TOXICITY

The sodium silicates are generally nontoxic. In water, their solutions are strongly basic, corrosive, and will cause irritation to the skin and respiratory system.[1662]

3. OTHER HAZARDS

When dissolved in water, the silicates are strongly alkaline and will attack aluminum.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, and Transportation

Solutions of the silicates, due to their alkalinity, attack aluminum. There are no other special handling and storage problems. The silicates may be shipped in solution in drums or dry in bags or fiber drums. There are no Department of Transportation (DOT) shipping regulations covering the silicates.[0766]

Disposal/Reuse

Industrially contaminated materials will probably not be considered for reprocessing for reuse based on economic consideration. The safe disposal of the sodium silicates is defined in terms of the recommended provisional limits in the atmosphere and in water and soil. These recommended provisional limits are as follows:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Sodium Silicate	0.02 mg/M^3*	0.01 TLV

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Sodium Silicate	0.10 mg/l*	Stokinger & Woodward Method

*Estimated

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The disposal of the sodium silicates is both simple and effective. The silicates are dissolved in water, acidified with 6M-HCl and allowed to stand for at least a day. The liquid is decanted into another container, neutralized, diluted, and discharged into a sewer or stream. The sludge (silica gel) is added to a landfill.[0095]

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The sodium silicates have been classified on a preliminary basis as probable candidate waste stream constituents for municipal disposal. Based on the disposal process described in Section 5, it may be concluded that waste treatment for the sodium silicate can be handled adequately locally and no consideration for National Disposal Site treatment is warranted.

7. REFERENCES

0095. Manufacturing Chemists Association. Laboratory waste disposal manual. 2d ed. Washington, 1969. 176 p.

0776. Sax, N. I. Dangerous properties of industrial materials. 2d ed., New York, Reinhold Publishing Corporation, 1957. 1,467 p.

0955. Sittig, M. Inorganic chemical and metallurgical process encyclopedia, Park Ridge, New Jersey, Noyes Development Corporation, 1968. 883 p.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sodium Silicates (402)

IUC Name

Common Names Water Glass

Structural Formula

NaO . $XSiO_2$ (X=2,3,4,5)

Molecular Wt. Not a fixed composition   Melting Pt.   Boiling Pt.

Density (Condensed) @   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water miscible   Hot Water miscible   Ethanol miscible

Others:

Acid, Base Properties strongly alkaline in aqueous solution

Highly Reactive with Gels form below pH 3 in water

Compatible with

Shipped in Paper bags, drums, tank trucks as solution(1)

ICC Classification None(1)   Coast Guard Classification None(1)

Comments

References (1) 1492

PROFILE REPORT

Strontium (410)

1. GENERAL

Kirk-Othmer[1433] reports that there is no known commercial use for strontium metal. World annual production is approximately 1,000 lb, which currently sells for $10.80/lb. At this price concentrated waste is a very attractive candidate for purification and recycling. The single primary North American producer and distributor is Dominion Magnesium, Ltd., Toronto, Canada,[0602,1433] who report that they generate no strontium waste. Their principal customer is a secondary distributor, Ventron Corporation, Beverly, Massachusetts,[0601] who purchase about 200 lb annually. They report that this quantity is broken down and sold in 10 to 15 lb lots to various research laboratories scattered throughout the country.

2. TOXICOLOGY

No toxicological information pertaining to strontium metal was found in the open literature and the 1971 HEW Toxic Substances Annual List[1312] does not list strontium as a toxic substance. It is suggested that strontium probably resembles calcium physiologically and that it only represents a toxicological hazard as the radioactive isotope strontium 90.

3. OTHER HAZARDS

Strontium resembles calcium chemically. It reacts with water to release hydrogen, which represents a fire and explosive hazard in itself, and form $Sr(OH)_2$ which is caustic. Metallic strontium represents a moderate fire hazard when in the form of dust and exposed to direct flame.

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4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Strontium wastes resulting from occasional laboratory use of small portions (generally less than 1 lb) of the metal are chemically reacted with water whereupon small amounts of hydrogen are evolved and the hydroxide is formed. The hydrogen is generally evolved in small quantities at sufficiently slow rates so that it is immediately diluted with room air and vented to the atmosphere in concentrations well below its flammability limits. The hydroxide [$Sr(OH)_2$] is then further diluted with water and washed down the drain. The $Sr(OH)_2$ in solution in the sewer system is very dilute and causes no problems.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

The practice of conversion of metallic strontium to strontium hydroxide utilizing water addition with subsequent dispersion of evolved hydrogen (in concentrations well below its flammability limit) to the atmosphere and the hydroxide to the sewer system is judged to be an adequate method of disposal.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Because of the small quantities of waste involved, the lack of toxicological hazard, and the simplicity of the disposal technique, metallic strontium is not judged to a candidate waste stream constituent requiring National Disposal Site treatment.

7. REFERENCES

0601. Personal communication. Mr. Fraser, Ventron Corporation, to M. Appel, TRW Systems, Feb. 10, 1972.

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1433. Kirk-Othmer encylcopedia of chemical technology. 2d ed. 22 v. and suppl. New York, Interscience Publishers, 1963-1971.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name

IUC Name STRONTIUM (410)

Common Names STRONTIUM

Structural Formula

Sr

Molecular Wt. 87.63 Melting Pt. 770 C Boiling Pt. 1380 C

Density (Condensed) 2.6 g/cc @ 20 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

10 mm @ 898 C

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Moderate (dust) Upper

Explosive Limits in Air (wt. %) Lower Moderate (dust) Upper

Solubility

Cold Water reacts to form $Sr(OH)_2 + H_2$ Hot Water reacts Ethanol slightly

Others: NH_4OH

Acid, Base Properties basic

Highly Reactive with water to evolve H_2

Compatible with Most metals

Shipped in metal drums or barrels not exceeding 25 lb net

ICC Classification flam. solid Coast Guard Classification

Comments container contents must be labeled if shipped over water Sec. 73.153, 73.154

PROFILE REPORT

Taconite Tailings (419)

1. GENERAL

The processing of taconite follows the classic extractive metallurgical method of crushing, grinding and separation (in this case by magnetic and hydraulic methods). The concentrates are then mixed with small amounts of clay and pelletized for shipment to iron smelters while the tailings, approximately two-thirds of the input ore, are left for disposal. A flow sheet for the taconite concentration portion of the Reserve Mining Company's operation at Silver Bay, Minnesota, which is fairly typical of today's taconite concentration plants, is presented (Figure 1).

As described by Aleshin and Schwartz,[0169] taconite ore averages 27 percent iron and 48 percent silica. The Mesabi range of Minnesota is the largest producer in the United States and annually produces some 66 million tons of tailings.

Concentrates contain some 99+ percent of the magnetic iron in the ore and the magnetic portion of the ore constitutes some 70 percent[1975] of the total iron content.

As previously noted, some two-thirds of the original ore is disposed of as tailings. Both coarse and fine tailings are produced by the concentration operation with some 90 percent of the ore being ground to -325 mesh. The tailings contain approximately 8 percent iron and a remainder, which is primarily the original siliceous gangue. "Some lime[0169] (1 lb/ton of tailings solids) or a proprietary cationic flocculating agent (1/8 ppm of pulp) are currently used to thicken the effluent from the concentrator to about 45 percent solids."

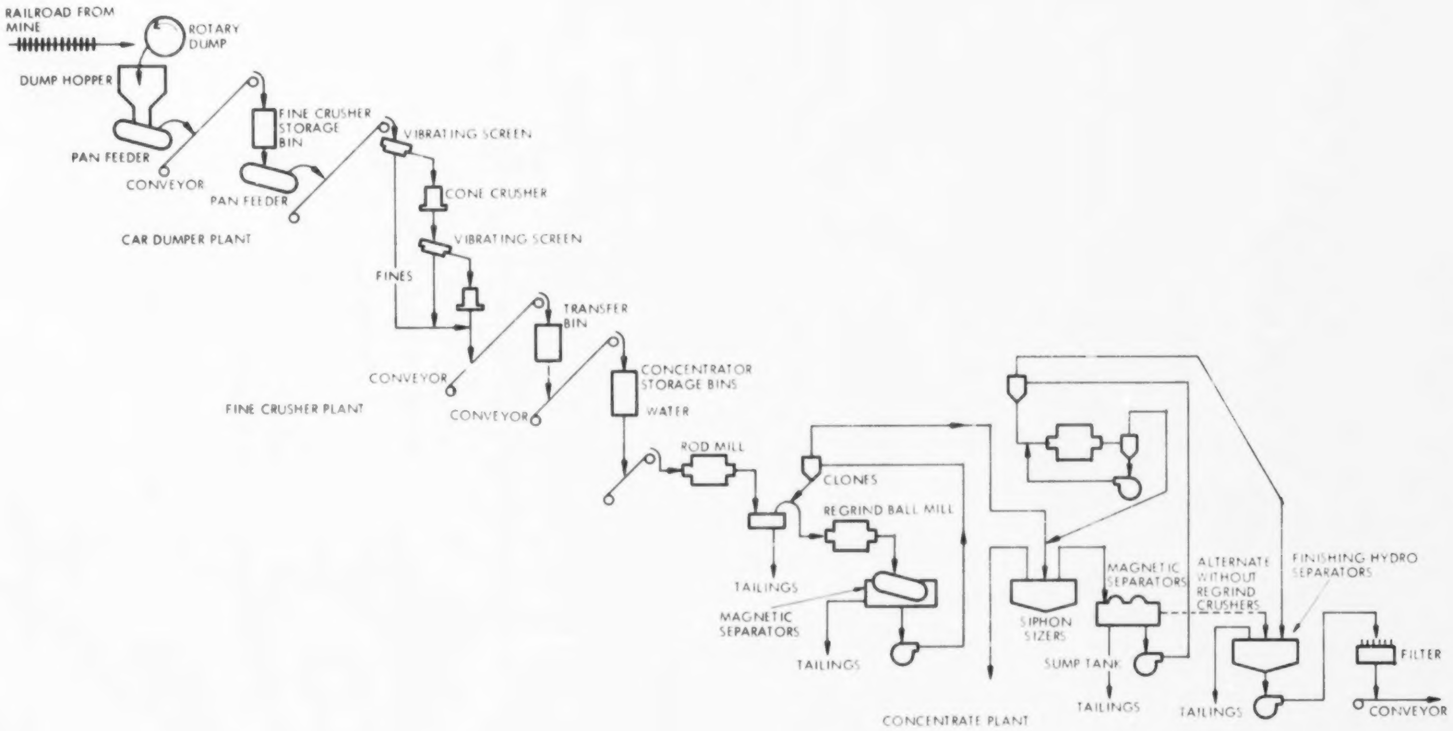
RAILROAD FROM MINE
ROTARY DUMP
DUMP HOPPER
PAN FEEDER
CONVEYOR
FINE CRUSHER STORAGE BIN
PAN FEEDER
CAR DUMPER PLANT
VIBRATING SCREEN
CONE CRUSHER
VIBRATING SCREEN
FINES
TRANSFER BIN
CONVEYOR
FINE CRUSHER PLANT
CONVEYOR
CONCENTRATOR STORAGE BINS
WATER
ROD MILL
CLONES
REGRIND BALL MILL
TAILINGS
MAGNETIC SEPARATORS
TAILINGS
CONCENTRATE PLANT
SIPHON SIZERS
MAGNETIC SEPARATORS
SUMP TANK
TAILINGS
ALTERNATE WITHOUT REGRIND CRUSHERS
FINISHING HYDRO SEPARATORS
TAILINGS
FILTER
CONVEYOR

Figure 1. Reserve Mining Company; Silver Bay Operation[2488]

2. TOXICOLOGY

Taconite tailings constitute a negligible toxicological hazard.

3. OTHER HAZARDS

Although taconite tailings present no toxicological hazard, they do constitute an environmental problem on the basis of two elemenst: (1) the sheer volume of the materials involved and (2) the dust problems encountered because of the fineness of the material.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Taconite tailings are presently disposed of by collection in tailings ponds (see Profile Report on Copper [275] Lead and Zinc [276] tailings) or, in one major case, by discharging the tailings into Lake Superior. The discharge into the lake was premised on a phenomenon known as the "heavy density current".[2487] As a result the discharge waters carry the tailings, which are heavier than the surrounding waters, into an area off shore where the lake depth is approximately 900 feet. It is indicated that the density of tailings in the waters discharged is 14,000 milligrams per liter.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Of the two disposal methods described in Section 4 of this report, only that of ponding is judged to be an acceptable method. The acceptability of the discharge of tailings into large potable water sources has not been determined. The discharge should be curtailed until the environmental effects of this practice are determined.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Because of the negligible toxicological effect, taconite tailings are not considered candidates for National Disposal Sites.

The recommendations for research and development to alleviate the environmental effects contained in the Profile Report on Copper (275), Lead and Zinc (276) Tailings also apply to taconite tailings. The disposal of tailings into bodies of water is presently in litigation questioning the environmental damage caused by this method.

7. REFERENCES

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1975. U.S. Bureau of Mines. Mineral facts and problems. Bulletin No. 650, 1970.

2487. Environmental Reporter. State of Minnesota vs. the Reserve Mining Company. 1972.

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PROFILE REPORT

Thallium (430) and Thallium Sulfate (431)

1. GENERAL

Production

There is one producer of thallium and thallium sulfate (Tl_2SO_4) in the United States, the American Smelting and Refining Company, Denver, Colorado.[1433, 2179, 2239, 2182] Its thallium department "operates on a very intermittent basis, having produced thallium in five short campaigns over the past twenty years. The department is not now in operation and is not scheduled for the foreseeable future."[2242]

Thallium is produced as a byproduct of the production of cadmium, which, in turn is produced as a byproduct of the production of zinc. The zinc dross remaining from the smelting of lead and zinc sulfide ores is leached with sulfuric acid to solubilize the cadmium and thallium, which is present in concentrations ranging from several ppm to 2000 ppm in the dross. The solution is electrolyzed to produce a cadmium-thallium alloy containing 5 to 20 percent thallium. This alloy is then solubilized as the hydroxides by the addition of hot water, and the cadmium is then precipitated by the addition of sodium bicarbonate. The filtrate is then treated with hydrogen sulfide to precipitate thallous sulfide, which in turn is dissolved in sulfuric acid. Electrolysis of the thallous sulfate solution yields pure thallium metal. The commercial sulfate is made by redissolving this metal in sulfuric acid and crystallizing from the saturated solution.[1287, 1433, 2239, 2242, 2240]

Use

Historically, thallium and thallium sulfate have been used as depilatories and in rodenticides and insecticides. However, their extreme toxicity has caused the U.S. Food and Drug Administration and the

U.S. Department of Agriculture to ban their use for these purposes. Customers for thallium sulfate must furnish an affidavit stating that the material will not be used for rodenticide or insecticide manufacture. [1433, 2242]

These were the only uses for these materials, so that currently there is no commercial use of any significant extent. Parts per billion quantities of thallium have been used as dopants in NaI crystals for γ-ray scintillation counting and the U.S. Army is experimenting with Hg-Tl alloys for arctic thermometers, since the eutectic temperature of -59 C is 20 C lower than the freezing point of pure mercury.

In the first seven months of 1972, total thallium metal sales amounted to 10 lb, while thallium sulfate sales were 90 lb. [2242] Definite information is not available with regard to the ultimate disposition of these sold materials, but it has been reported that thallium is present in minor concentrations in various electrical connections, solders and fusible alloys. [1288] In 1964 it retailed for $7.50/lb.

2. TOXICOLOGY

Health and Safety Standards

The Threshold Limit Value (TLV) for thallium and thallium compounds is 0.1 mg/m^3. [0766] On contact with the skin, thallium and thallium compounds are readily solubilized by formation of the chloride, which then penetrates into the body. The toxicity and epidemiology of thallium and its compounds are not influenced by the mode of entry. [2238,2241]

Epidemilogy [2238,2241,2180]

The HEW 1971 Annual List of Toxic Substnaces [1312] reports the LD_{50} of 29 mg/kg in the mouse and 15.8 mg/kg in the rat for Tl_2SO_4 administered orally. Since thallium rapidly solubilizes on contact with skin and clinical symptoms seem independent of mode of entry, it may be concluded that the pure element or other compounds would give approximately the same results.

The most dramatic clinical symptom is alopecia (baldness), and it is for this very property that is was widely used in patent medicine applications until its toxicity forced it off the market. It diffuses readily through the body and produces widespread damage to the nervous system and the gastrointestinal tract. Respiratory failure and cardiac depression have been noted in laboratory animals.

Diagnosis is complicated by the fact that it takes several days for symptoms to appear. The mechanisms are unknown, but as with most heavy metals, enzyme-poisoning is suspected. The metal is eventually excreted via the kidney, but removal is very slow, so that it may be classified as a "somewhat cumulative" poison. There is no known antidote; i.e., no way has been found either to precipitate and immobilize it within the body or to hasten its elimination through the kidney.

3. OTHER HAZARDS

Thallium and thallium compounds are relatively unreactive. On heating fumes of the toxic, water-soluble Tl_2O are generated.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

Thallium and thallium sulfate are extremely toxic chemicals and the use of full protective clothing, goggles, and respirators is recommended in their handling. If clothing has been contaminated, it should be removed as soon as possible and the skin should be immediately washed with plenty of water and soap.

Thallium and thallium sulfate should be stored in cool, dry, well-ventilated places, and away from any area of high fire hazard. The producer stores the refined thallium and thallium sulfate in Denver, Colorado in a prefab steel structure with asphalt paving and in a brick building with a concrete floor.[2242]

Thallium metal is marketed as sticks, 3/8-in.-diameter by 9 in., weighing approximately 6-1/2 oz, or as ingots, 2 in. by 3-9/16 in. by 7-9/16 in., weighing approximately 20 lb. These shapes are sealed in polyethylene plastic and packed in wooden boxes as required. Thallium sulfate is sold in 2-1/2-lb amber glass bottles and shipped in sawdust-filled mailing tubes packed in wooden boxes. Twenty-five-lb orders may be packed in polyethylene-lined steel pails, 9 in. by 7-1/2 in.[2242]

Thallium and thallium sulfate are classified as Class B poisons by the Department of Transportation (DOT) and the rules and regulations governing their transportation are given in the Code of Federal Regulations (CFR) Title 49-Transportation, Part 71-90.[0278]

Disposal/Reuse

The zinc dross containing the trace quantities of thallium (2 to 2000 ppm) is not disposed of; rather it is stockpiled in anticipation of future use. Since thallium is not currently in production, no waste is being generated from the refining process. Previous experience indicates that airborne emissions from thallium production are nil, and the liquid effluent averages <0.1 ppm on delivery to the waste storage facility. The small amounts (<200 lb annually) of thallium and thallium compounds used commercially are widely dispersed in very small quantities. For the disposal of wastes, which incidentally contain small amounts of thallium and thallium sulfate, the acceptable criteria for their release into the environment are defined in terms of the following provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Thallium	0.001 mg/M^3	0.01 TLV
Thallium Sulfate	0.001 mg/M^3 as Tl	0.01 TLV for Tl

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Thallium	0.005 ppm (mg/l)	Stokinger and Woodward Method
Thallium Sulfate	0.005 ppm (mg/l) as Tl	Stokinger and Woodward Method

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - Stockpiling of Zinc Dross Containing Trace Quantities of Thallium

This may be judged satisfactory. There is no evidence that thallium from this stockpile has become airborne or has leached into any ground water.

Option No. 2 - Production of Thallium from Stockpiled Zinc Dross

The procedures used in the past may be judged satisfactory, as can be seen from the following comparison:

	Tl Released[2242]	TLV[0766]
airborne emission	nil	0.1 mg/M^3
liquid effluent	<0.1 ppm	0.5 ppm

If and when production resumes, care must be taken to minimize worker exposure in the refining operation. The extractive metallurgy is relatively straightforward and well within the state-of-the-art, so worker protection should not present any untoward technical or economic problems.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The handling, storage, and transportation of thallium and thallium sulfate are adequate at present and for the foreseeable future. If and when production resumes, worker exposure in the refining operation should be carefully monitored. Health and safety should not prove a problem.

Information on the disposal of incidental quantities of thallium after use is not available. While no incidences of thallium poisoning have been uncovered, it is nevertheless advisable for these disposals to be pinpointed in location and quantity. Additional education of users with regard to the hazards of thallium and thallium sulfate may prove desirable. Small quantities may easily be disposed of by sealing in polyethylene bags and burying in Class 1 landfills, i.e., landfills with no access to ground water.

Thallium and thallium sulfate can be handled quite adequately at the industrial level and are therefore not candidate waste stream constituents for national disposal.

7. REFERENCES

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0766. Sax, N. I. Dangerous properties of industrial materials. 3d ed. New York, Reinhold Publishing Corp., 1968. 1,251 p.

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1433. Kirk-Othmer encyclopedia of chemical technology. 2d ed. 22 v. and suppl. New York, Interscience Publishers, 1966 899 p.

2179. Personal communication. M. Coats, American Smelting and Refining Co. to M. Appel, TRW Systems, July 24, 1972. Thallium and thallium sulfate.

2180. International Occupational Safety and Health Information Centre. Four citations on thallium. CIS-34, CIS-40, CIS-41, CIS-67, no date.

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2239. Prater, J. E., et al. Recovery of thallium from smelter products. U.S. Bureau of Mines Report RI-4900. 1952.

2240. Teats, R. Process for recovering thallium/treating sulfate solutions of thallium and cadmium. U.S. Patent Numbers 2,060,453 and 2,011,882. Nov. 10, 1936 and Aug. 20, 1935.

2241. Pfizer Laboratories. Thallium poisoning. Pfizer Spectrum, 6(20):558, 1958.

2242. Personal communication. M. Coats, American Smelting and Refining Co. to M. Appel, TRW Systems, August 10, 1972.

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Thallous Sulfate

IUC Name Thallium Sulfate (431)

Common Names

Structural Formula

Tl_2SO_4

Molecular Wt. 505 (1)   Melting Pt. 632 C (1)   Boiling Pt. decomposes

Density (Condensed) 6.77 g/cc @ 20 C   Density (gas) ____ @ ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____   ____ @ ____   ____ @ ____

Flash Point ____   Autoignition Temp. ____

Flammability Limits in Air (wt %)   Lower ____   Upper ____

Explosive Limits in Air (wt. %)   Lower ____   Upper ____

Solubility

Cold Water 4.87 g/100 ml   Hot Water 15.57 g/100 ml   Ethanol ____

Others: ____

Acid, Base Properties ____

Highly Reactive with ____

Compatible with ____

Snipped in metal drums, wooden barrels either lined with paper or tongue-and-grooved

ICC Classification Poison B; poison label, 200 lb   Coast Guard Classification Poison B; poison label

Comments

Code of Federal Regulations, Sec. 73.364 and 73.365

References (1) 1433

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 430

IUC Name Thallium (430)

Structural Formula

Tl

Common Names

Molecular Wt. 204 (1)   Melting Pt. 303 C (1)   Boiling Pt. 1457 C

Density (Condensed) 11.85 g/cc @ 20 C   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

1 mm @ 825 C   @   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower moderate (as dust)   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water insoluble   Hot Water insoluble   Ethanol insoluble

Others: HNO_3, H_2SO_4, slightly in HCl

Acid, Base Properties slightly basic

Highly Reactive with

Compatible with

Shipped in metal drums, wooden barrels either lined with paper or tongue-and-grooved

ICC Classification Thallium salts, solid: Poison B; poison label, 200 lb   Coast Guard Classification Thallium salts, solid: Poison B; poison label 200 lb

Comments

Code of Federal Regulations, Sec. 73.364 and 73.365

References (1) 1433

PROFILE REPORT

ZINC COMPOUNDS

Zinc Chloride (456), Zinc Nitrate (459), Zinc Permanganate (461), Zinc Peroxide (462), Zinc Sulfide (463)

1. GENERAL

The zinc compounds with specific exceptions, do not have serious toxicities and can be adequately handled by current industrial or commercial treatment methods. These compounds will be discussed as a class in this Profile Report and important exceptions to general remarks will be cited.

Zinc chloride is the second most commercially important zinc compound after zinc oxide. Most, if not all, of the zinc chloride produced in the United States is derived from secondary zinc sources such as zinc dross and sal skimmings. They are normally treated with muriatic acid and the product solution is filtered off. The nearly dry residue is then chlorinated. The resulting, additional zinc chloride is leached with water and added to the original filtrate. Concentration and purification follows. Zinc chloride is used in combination with other compounds as a wood preservative and fire proofing lumber. It is used as a deodorant, in disinfectants, embalming fluids, as a fungicide, in the manufacture of vulcanized fiber and parchment paper, as a dyeing mordant, in oil refineries, galvanizing and manufacture of dry batteries.[2377] Zinc is the largest plating commodity and zinc chloride is widely used in the industry. Production of $ZnCl_2$ in the United States was 28,000 tons in 1966.

Zinc sulfide is used as a pigment in paints and plastics. It exhibits phosphorescence when very pure and is used in cathode ray tubes, TV picture tubes and luminous watch dials. It is insoluble in water and does not constitute a hazard unless exposed to acids.

Zinc nitrate is believed to be made by reacting a zinc source with nitric acid. The pattern of purchase by industries indicate that it is used in textile dyeing and engraving.[2360] Its consumption for all purposes was not available.

Zinc permanganate is classed as a rarely used compound by its sole commercial manufacturer. Its use is believed to be confined to pharmaceuticals as an oxidizing agent where it is much more soluble than the commonly used potassium permanganate. Sales are certainly less than 1,000 lb annually and probably less than 50 lb.[2361]

Zinc peroxide is used in pharmaceuticals and as a curing agent for polysulfides. It is consumed in the reactions where it is added and is not believed to occur anywhere as a specific waste. It slowly decomposes to zinc oxide. In polymer formulation the zinc residues are of course bound up and present no significant hazard.

Physical Properties

The available physical and chemical properties of the materials discussed in this Profile Report are included in the attached worksheets.

2. TOXICITY

Zinc compounds in general are not inherently very toxic. The general toxic effects of the zinc compounds are noted in three distinct areas of exposure: inhalation, ingestion and skin contact.

Inhaled zinc compounds can cause a mild reaction called "metal fume fever," "brass chills,", "oxide shakes" and other colorfully descriptive illnesses. Zinc chloride irritates the mucosa probably because HCl is liberated from hydrolysis. All these symptoms readily disappear when airborne zinc is controlled.

Small amounts of zinc have a metallic taste and can cause illness and digestive tract disorders. Small amounts of concentrated zinc peroxide or permanganate can also cause localized tissue inflamation.

Skin contact with these compounds may result in rare and minor symptoms of zinc poisoning, but in general the epidermis is resistant to zinc compounds and any localized disorders are most likely to be caused by the anion.

The recommended Threshold Limit Value (TLV) for zinc chloride fume is 1 mg per cubic meter of air.[0225] The drinking water standards have been set at 15 mg per liter.

3. OTHER HAZARDS

Zinc nitrate, zinc peroxide and zinc permanganate are moderately strong oxidizers. They should not be allowed to contact reducing material or a fire could result. No other hazards have been found to exist.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

The zinc compounds can be handled with relative ease. These materials should be handled and stored in a well ventilated area. The containers should not be agitated when open, and when stored, should be sealed to prevent the hazard of airborne particles. The nitrates, peroxides and permanganates are classed as oxidizing materials and require yellow labels. The producers of these material can supply details on container information but in general fiber drums are sufficient for these materials.

Disposal/Reuse

Zinc chloride can be recovered from plating operations or other processes when the waste stream is segregated or free from other contaminants. However, the proportion of firms who are recovering zinc is estimated to be small.[2350] The commercial applications of zinc nitrate, peroxide and permanganate indicate that they will be consumed, or transformed to the degree that they are no longer easily recoverable. However, the use of sulfides to precipitate pigment grade zinc sulfide from zinc-containing waste streams should always be considered whenever it is technically possible and economically justifiable.[2359,2361]

For the release of these zinc compounds into the environment, the acceptable criteria are defined in terms of the following provisional limits:

Contaminant in Air	Provisional Limit	Basis for Recommendation
Zinc Chloride	0.01 mg/M^3	0.01 TLV
Zinc Nitrate	0.05 mg/M^3 as HNO_3	0.01 TLV for HNO_3
Zinc Permanganate	0.05 mg/M^3 as Mn	0.01 TLV for Mn
Zinc Peroxide	0.014 mg/M^3 as H_2O_2	0.01 TLV for H_2O_2
Zinc Sulfide	0.15 mg/M^3 as H_2S	0.01 TLV for H_2S

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Zinc Chloride	5 ppm (mg/l) as Zn	Drinking Water Standard
Zinc Nitrate	5 ppm (mg/l) as Zn	Drinking Water Standard
Zinc Permanganate	5 ppm (mg/l) as Zn	Drinking Water Standard
Zinc Peroxide	5 ppm (mg/l) as Zn	Drinking Water Standard
Zinc Sulfide	5 ppm (mg/l) as Zn	Drinking Water Standard

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Option No. 1 - By-Product Recovery and Recycling

Effluent streams from industries such as metal finishing and electroplating often contain zinc wastes that can be readily recovered as a by-product. Equipment which can be utilized to concentrate a stream for reuse include reverse osmosis, multiple effect evaporation, and ion exchange. In some cases usable water is also recovered. Precipitation of zinc sulfide, a useful pigment, is also possible. Recycling and by-product recovery is an acceptable and favored treatment option inasmuch as it reduces overall waste loads.

Option No. 2 - Destructive Precipitation

The use of lime, soda ash and similar materials to render waste streams alkaline, leading to the precipitation of heavy metal hydroxide sludges, is in widespread use today. The sludges present a handling and disposal problem which has been previously discussed in the Profile Reports on the chromates, nickel compounds, copper compounds, (21,22, etc.). The procedure produces effluents with satisfactory zinc levels and is adequate for waste streams where recovery is not feasible.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The treatment of zinc compounds can be carried out adequately at the site of generation and hence the need for centrally treating these compounds is not indicated. A facility for destructive precipitative by pH adjustment has been recommended for the treatment of wastes generated within National Disposal Sites. This facility could also be used to handle non-routine shipments of zinc wastes to National Sites.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Zinc Chloride (456)

IUC Name

Common Names Butter of Zinc[3]

Structural Formula

$ZnCl_2$

Molecular Wt. 136.30[1]

Melting Pt. 262 C[1]

Boiling Pt. 732 C[1]

Density (Condensed) 2.91 @ 25 C[1]

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

1 mm @ 428 C[1]

@

@

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 432 g/100 cc

Hot Water 615 g/100 cc

Ethanol 100 g/100 cc

Others: ether

Acid, Base Properties Aqueous solution is acid to litmus

Highly Reactive with

Compatible with

Shipped in

ICC Classification

Coast Guard Classification

Comments

References (1) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Zinc Nitrate Trihydrate (459)

IUC Name

Common Names

Structural Formula

$Zn(NO_3)_2 \cdot 3H_2O$

Molecular Wt. 243.43(1) Melting Pt. 45.5 C(1) Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 327.3 g/100 cc @ 40 C(1) Hot Water Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in fiber drums - poly lined

ICC Classification oxidizing material, yellow label, 100 lb Coast Guard Classification same

Comments

References (1) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Zinc Nitrate Hexahydrate (459)

IUC Name

Common Names

Structural Formula

$Zn(NO_3)_2 \cdot 6H_2O$

Molecular Wt. 297.47(1)

Melting Pt. 36.4 C(1)

Boiling Pt. $-6H_2O$ 105-131(1)

Density (Condensed) 2.065 g/cc @ 14 C(1)

Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point

Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 184.3 g/100 cc @ 20 C(1)

Hot Water infinitely sol.(1)

Ethanol very soluble(1)

Others:

Acid, Base Properties solution is acid to litmus, pH of 5 percent aq. soln. is 5.1(3)

Highly Reactive with

Compatible with

Shipped in

ICC Classification oxidizing material, yellow label, 100 lb(2)

Coast Guard Classification same(2)

Comments

References
- (1) 1570
- (2) 0766
- (3) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Zinc Permanganate (461)

IUC Name

Common Names

Structural Formula

$Zn(MnO_4)_2 \cdot 6H_2O$

Molecular Wt. 411.33(1) Melting Pt. $-5H_2O$ @ 100 C(1) Boiling Pt.

Density (Condensed) 2.47 @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 33.3 g/100 cc(1) Hot Water very soluble(1) Ethanol decomposes(1)

Others: decomposes in acids(1)

Acid, Base Properties

Highly Reactive with reducing agents

Compatible with

Shipped in

ICC Classification oxidizing mtl. yellow label, 100 lb(2) Coast Guard Classification same

Comments Chrystaline form deliquesces(1)

References (1) 1570

(2) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Zinc Peroxide (462)

IUC Name

Common Names ZPO, zinc superoxide

Structural Formula

$ZnO_2 \cdot 1/2H_2O$

Molecular Wt. 106.38(1) Melting Pt. $-O_2$ with vac.(1) Boiling Pt.*

Density (Condensed) 3.00(1) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water slowly decomposes(1) Hot Water decomposes(1) Ethanol decomposes(1)

Others: decomposes in ether, acetone(1)

Acid, Base Properties

Highly Reactive with heat or reducing materials(2) explodes at 212 C(2)

Compatible with (Not dangerous unless mixed with combustibles)(2)

Shipped in fiber drums, no liner required

ICC Classification yellow label oxidizing material, 100 lb Coast Guard Classification same

Comments Toxicity similar to ZnO

coml. prod. 50 to 60 percent ZnO_2 remainder is ZnO

*Decomposes above 150 C(3)

References (1) 1570

(2) 0766

(3) 1492

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Zinc Sulfide (463)

IUC Name

Common Names Wurtzite(2)

Structural Formula

ZnS

Molecular Wt. 97.45(1)   Melting Pt. 1850 C @ 150 atm(1)   Boiling Pt. sublimes at(1) 1183 C

Density (Condensed) 4.087(1) @   Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@   @   @

Flash Point   Autoignition Temp.

Flammability Limits in Air (wt %)   Lower   Upper

Explosive Limits in Air (wt. %)   Lower   Upper

Solubility

Cold Water insoluble(1)   Hot Water insoluble(1)   Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification   Coast Guard Classification

Comments

References (1) 1570